Sulfur-bonded thiophenes in organometallic rhenium complexes
and adsorption of isocyanides on gold

by Mitchell Joe Robertson

Ph.D. thesis submitted to Iowa State University
Ames Laboratory, U. S. DOE

Iowa State University
Ames, Iowa 50011

Date Transmitted: August, 1993

Prepared for the U. S. Department of Energy
Under contract no. W-7405-eng-82.

1993

rb

RECEIVED

SEP 27 1993

OSTI

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

AVAILABILITY:

To DOE and DOE contractors: Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

prices available from: (615) 576-8401
FTS: 626-8401

To the public: National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

DEDICATION

To my mom and dad

TABLE OF CONTENTS

RECEIVED

SEP 2 1994

	Page
GENERAL INTRODUCTION. ADSORPTION OF SMALL MOLECULES ON GOLD	1
 PAPER 1. SYNTHESIS AND PROTONATION OF THE BRIDGING BENZO[b]THIOPHENE (BT) COMPLEXES [Cp'Re(CO) ₂](η^2 : η^1 (S)- μ_2 -BT)[Re(CO) ₂ Cp'']	19
ABSTRACT	20
INTRODUCTION	21
EXPERIMENTAL	23
RESULTS AND DISCUSSION	39
CONCLUSION	51
REFERENCES	52
 PAPER 2. SULFUR-COORDINATED THIOPHENE AND BENZO[b]THIOPHENE IN Cp(NO)(PPh ₃)Re(thiophene) ⁺ COMPLEXES: CONVERSION TO THIENYL AND THIENYLCARBENE COMPLEXES	55
ABSTRACT	56
INTRODUCTION	57
EXPERIMENTAL	59
RESULTS AND DISCUSSION	68
CONCLUSION	80
REFERENCES	82

PAPER 3. ADSORPTION OF ARYL AND ALKYL ISOCYANIDES ON POWDERED GOLD	86
ABSTRACT	87
INTRODUCTION	88
EXPERIMENTAL	91
RESULTS AND DISCUSSION	94
CONCLUSION	109
REFERENCES	110
GENERAL SUMMARY	114
ADDITIONAL REFERENCES	116
ACKNOWLEDGMENT	119

GENERAL INTRODUCTION. ADSORPTION OF SMALL MOLECULES ON GOLD

Explanation of Dissertation Format

This dissertation contains results of research I have conducted in two different areas: 1) organometallic synthesis and reactivity 2) organometallic surface chemistry. In the synthesis and reactivity studies, sulfur coordination of thiophene and benzo[b]thiophene to the metal center in organometallic rhenium complexes is examined. In the surface chemistry studies, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is used to analyze the adsorption of several isocyanides on the surface of gold powder. The results are compared and contrasted to known organometallic chemistry.

This dissertation contains a general introduction and three papers. The general introduction is a literature review of the adsorption of small molecules on gold, and does not consider most electrochemical and interfacial studies using gold as a substrate. The following three papers contain the results of my research as it was or will be submitted for journal publication. Literature citations, tables, and figures pertain only to the papers in which they are included. Following the third paper is a general summary and the additional references cited in the general introduction.

Introduction

A quick review of chemical literature will show that the chemistry of gold compounds is not as extensive as for most other transition metals. With the exception of cluster chemistry, almost all known gold compounds contain gold that is formally in the Au(I) or Au(III) oxidation state. The lack of chemistry reported for gold is probably due to the low coordination number for Au(I) and Au(III), and therefore a fewer number of compounds, and most certainly due to the low reactivity of gold metal itself. Gold metal is inert and resistant to oxidation.

Due to its inert nature, gold is often used in electrochemical studies, so the electrochemistry of gold has been extensively developed. Gold is also used as a substrate in colloidal and interfacial solution chemistry for the same reason. However, the surface chemistry of gold involving the adsorption of small molecules from the gas phase to the solid gold surface has developed randomly and sporadically.

This review will examine reports published in the chemical literature pertaining to small molecules adsorbed on a gold surface. Most of the studies were carried out under ultrahigh vacuum (UHV) in the past several decades. The gold substrates were polycrystalline gold films, supported gold particles, or a preferentially exposed crystal face: Au(100), Au(110), or Au(111). Modern UHV techniques and instrumentation were often employed in these studies. A brief explanation of the major techniques is summarized in Table 1.

Table 1. UHV techniques.¹

	<u>technique</u>	<u>atomic process</u>	<u>type of information</u>
LEED	low energy electron diffraction	elastic backscattering of electrons	surface structure
AES	Auger electron spectroscopy	energy of an ejected Auger electron induced by ejection of an inner electron with an electron beam	surface composition
TDS	thermal desorption spectroscopy	Adsorbates leave surface at characteristic temperatures	characterization of adsorption sites and adsorbed species
XPS	X-ray photoelectron spectroscopy	X-rays eject electrons from various atomic levels; the electron energy spectrum is measured.	surface composition and oxidation state
UPS	ultraviolet photoemission spectroscopy	same as XPS, but using UV light	surface composition and oxidation state
EELS	electron energy loss spectroscopy	incident electrons are scattered inelastically	identification of adsorbed species through their vibrational energy spectra
HREELS	high resolution EELS	same as EELS	same as EELS

Since there has been no methodical or comprehensive study of one particular molecule adsorbed on different surfaces, or of several molecules adsorbed on one specific surface, this review is organized into sections based on each individual adsorbate molecule. A summary of experimental results will be included in these sections.

CO

One of the first and most extensively studied molecules adsorbed on gold has been carbon monoxide (CO). The adsorption of CO has been studied on both single crystal and polycrystalline gold surfaces. Since the CO molecule can be easily monitored by infrared spectroscopy, some studies were performed before the advent of modern UHV techniques, often at ambient temperatures.

Infrared spectroscopy to study the adsorption of CO on gold was first used by Kavtaradze and Sokolova in 1962.² Their supported gold samples were prepared by reaction of Al_2O_3 with aqueous solutions of HAuCl_4 , with subsequent reduction of the sample by heating in H_2 gas. They observed a single strong absorption band at 2174 cm^{-1} , presumably due to the CO bonded perpendicular to the gold through the carbon atom.

Five years later, Guerra and Schulman studied the adsorption of CO on SiO₂-supported gold,³ which was also prepared from solutions of HAuCl₄. They observed a single weak band at $\sim 2075\text{ cm}^{-1}$. In later work,⁴ it was reported that the band position shifts towards 2100 cm^{-1} , depending on the sample reduction conditions.

Almost concurrently, Yates also reported an infrared study of CO adsorption on SiO₂-supported gold.⁵ He reported the $\nu(\text{CO})$ band at 2120 cm^{-1} and low coverages of CO; at higher coverages it shifted toward 2110 cm^{-1} . Also, he was able to show that the $\nu(\text{CO})$ band observed by Kavtaradze and Sokolova² could be produced by adsorbing CO on a gold sample that had not been completely reduced.

Bradshaw and Pritchard⁶ were the first investigators to report an infrared study of CO adsorption on evaporated gold films -- an unsupported gold sample. Unlike the aforementioned studies that were performed at room temperature, these adsorptions were carried out at 113 K. Still, a single band was again observed at 2120 cm^{-1} at low CO coverage, and it shifted to lower wavenumbers with increasing coverage.

In 1972, Kottke, Greenler, and Tompkins used an infrared reflection-absorption technique to successfully study CO adsorption on gold film.⁷ With this technique, they were able to observe adsorbed CO down to 5% monolayer coverage. Again, they observed a single $\nu(\text{CO})$ band at 2120 cm^{-1} at 0.01 torr of CO. When the CO pressure was increased to 20 torr, the band shifted lower to 2115 cm^{-1} , but it

shifted back up when the pressure was decreased. They surmised that at increasing coverage, some type of interaction between the adsorbed molecules was causing the band to shift; it was not due to a different type of adsorption site for the CO. By varying the CO pressure at constant temperature and measuring the intensity of the $\nu(\text{CO})$ band, an adsorption isotherm was produced. They estimated the isotheric heat of adsorption for CO on gold to be $E_{\text{ad}} = 13.1 \text{ kcal/mol}$. Using this technique, the workers were able to scan spectra down to 400 cm^{-1} ; however, they were unable to observe any gold-carbon (Au-C) stretching mode in this low wavenumber region that could be attributed to the gold-carbon bond.

An infrared study of CO adsorption on gold films in UHV was performed in 1986 by Dumas and coworkers.⁸ The sample consisted of a gold film deposited on a sapphire substrate. Interestingly, only films deposited at a substrate temperature $<290 \text{ K}$ were able to chemisorb CO. The CO was adsorbed at 2 K , and they observed a band at 2125 cm^{-1} at low coverages that move $10\text{-}15 \text{ cm}^{-1}$ lower with increasing coverage. The estimated maximum surface coverage of CO on the gold film was 0.6 monolayer.

Other UHV studies have confirmed the adsorption of CO on polycrystalline gold. Both UPS⁹ and photoemission studies¹⁰ have shown that CO chemisorbs at 77 K . Also, electrochemical techniques have been used to detect the change in work function of the surface of the gold film upon CO adsorption.¹¹ In this study, they observed that CO adsorbed reversibly at 17 K and CO pressures of 1.1×10^{-3} to 2×10^{-2}

torr. Here, the heat of adsorption for CO on gold was calculated to be $E_{ad} = 11.3 \pm .3$ kcal/mol.

Two UHV studies of CO adsorption on gold single crystal faces have been performed. On the Au(100) face,¹² many techniques were used to observe the adsorption from 81.5-260 K. Throughout this temperature range, CO did chemisorb, but there was no ordered CO structure on the surface. The CO did not induce any type of surface reconstruction, either. The adsorption energy for CO on the Au(100) face was estimated to be $E_{ad} = 14 \pm 1$ kcal/mol.

On the Au(110) face,¹³ the CO could not be stabilized on the surface down to 125 K, implying $E_{ad} < 8$ kcal/mol. When the surface was oxidized by the introduction of oxygen adatoms (discussed later), CO adsorption still could not be stabilized. However, the CO adsorption did react with O adatoms to form CO₂ in a low activation energy process ($E_a = 2$ kcal/mol).

CO₂

Carbon dioxide adsorption on the Au(110) face was studied under UHV conditions in tandem with CO adsorption.¹³ Like CO, CO₂ could not be stabilized on the clean or oxidized surface. Unlike CO (*vide supra*), the CO₂ did not react with surface adatoms, in this case to give a surface carbonate (CO₃) species, as was previously observed on the Ag(110) surface.¹⁴

O₂

There has been some confusion as to whether oxygen gas, O₂, will chemisorb to a gold surface. Most studies involving O₂ adsorption have been carried out almost exclusively under UHV conditions. While it is generally noted that the chemisorption of oxygen from the gas phase molecular state does not take place at room temperature,¹⁵ several research groups in the mid-1970's reported the chemisorption of O₂ on the Au(111) surface at elevated temperatures (373 - 773 K).^{16,17} Shrader later clarified his work by postulating that gold first dissociatively chemisorbed onto calcium atoms, a known impurity in his gold samples, with subsequent migration of the O adatoms from the calcium sites to gold sites.¹⁸ That same year, Eley and Moore reported: "There is ample evidence, from volumetric and surface potential measurements, that molecular oxygen does not adsorb on polycrystalline gold at 298 K."¹⁵ Still, in 1980, using LEED, AES, and EELS, Légaré, Hilaire, Sotto, and Maire reported that the adsorption of O₂ on clean surfaces becomes noticeable at T > 573 K.¹⁹ However, they also reported that the presence of calcium enhanced the adsorption. They also theorized that O₂ could dissolve into the bulk of the gold and segregate to the surface upon annealing the gold.

In the mid-1980's, the issue of oxygen adsorption was resolved. Two reports were published concurrently. Pireaux and coworkers²⁰ used electron spectroscopy techniques to determine that O₂ does not adsorb on clean Au(110) and Au(111) at O₂ pressures ranging from

10^{-10} - 10^{-5} torr and temperatures 100 - 800 K. Oxygen did adsorb when an impurity was present. Madix and coworkers²¹ used AES, XPS, and TDS to show that O_2 did not adsorb on clean polycrystalline gold for O_2 pressures up to 10^{-4} torr and temperatures 300 - 600 K. They showed that chemisorbed oxygen observed in earlier work by others was probably due to a very small and almost undetectable silicon impurity in the gold. The silicon diffuses from the bulk of the material to the surface upon heating and reacts with O_2 to form surface SiO_2 . Madix and coworkers later reported²² that O_2 did not dissociatively adsorb on clean Au(110) at temperatures from 300 - 500 K and O_2 pressures up to 1400 torr!

Oxygen adatoms can be placed on the surface of gold by exposing the gold sample to O_2 in proximity to a hot tungsten filament.²² These oxygen adatoms can recombine to desorb as O_2 at approximately room temperature or higher. The oxygen adatoms are also used to react with other adsorbates (*vide infra*).

H_2

The adsorption of H_2 on gold was studied briefly by Madix and coworkers as part of their O_2 adsorption studies.²² H_2 did not chemisorb on gold, but hydrogen adatoms could be deposited on the surface in the same manner as O adatoms. The H adatoms could recombine at 16 K to desorb H_2 . Hydrogen gas was also shown to react, though with very low probability, with O adatoms on the gold surface.

H₂O

The adsorption of H₂O on gold has been studied sporadically during the past several decades. Wells and Fort²³ first examined the adsorption of water on polycrystalline gold in 1972 by measuring the change in work function of the gold sample upon exposure to water vapor. They observed rapid physisorption and slow chemisorption. They broadly determined that $E_{ad} = 3-9$ kcal/mol for the physisorption of H₂O. The next year, Brundles and Roberts²⁴ utilized UPS to study the adsorption and determined that H₂O adsorbed molecularly at low temperatures and formed multilayers on the surface. By UPS, the adsorbed H₂O looked similar to gas-phase H₂O. The dissociative adsorption of H₂O was reported in 1975¹⁶ and 1977¹⁷, but like with O₂, it was later thought that the H₂O adsorption was due to impurities on the gold surface.

In 1989, the influence of intermolecular hydrogen bonding of the water molecules in the molecular adsorption of H₂O on Au(111) was examined.²⁵ The H₂O was adsorbed at 85 K, with an observed sticking probability close to one. Only molecular adsorption was observed, and multilayers did form. For H₂O, $E_{ad} = 10.5$ kcal/mol. It was noted that H₂O bound more strongly to itself than to the gold surface due to intermolecular hydrogen bonding. Presumably, the hydrogen bonding affected the desorption of H₂O from the gold sample.

H₂S

Kostelitz, Domange, and Oudar studied H₂S adsorption on Au(111), Au(100), and Au(110) using LEED and AES in 1973.²⁶ They found that H₂S does adsorb on each face to give sulfur atoms on the surface, albeit with different surface structures on the different faces. Much later, Jaffey and Madix studied H₂S adsorption on clean and sulfided Au(110).²⁷ H₂S adsorbed molecularly at 105 K with a sticking probability close to one up to the first monolayer. Interestingly, only about 2% surface sulfur atoms result from subsequent dissociative chemisorption of the H₂S. The H₂S was observed by TDS to desorb from four different states. An electron beam was used to induce further chemisorption of the physisorbed H₂S on the surface by initiating decomposition of the molecule. This form of chemisorption gave surface S atoms and S-H groups. The combination of these groups resulted in a fifth desorption state of H₂S from the surface.

HCOOH and HCOH

Formic acid adsorption on gold was first studied in 1983 using HREELS.²⁸ Adsorption on Au(110) was contrasted to adsorption on Au(111). The HCOOH was adsorbed at 100 K, where it physisorbed in multilayers, presumably with intense hydrogen bonding among molecules. The sticking coefficient of the formic acid on both gold surfaces was low. The samples were then heated to decompose the HCOOH. On the Au(110) face, the HCOOH simply desorbed and decomposed. However, on the Au(111) face, the HCOOH evolved into a

formic anhydride surface intermediate that formed other surface species, like formyl (HCOO), upon heating.

- Later, in 1985,²⁹ the difference in reactivity on the Au(110) and Au(111) surfaces was examined again. At 100 K, HCOOH physisorbed as a monolayer of dimers. These dimers contained a significant hydrogen-bonding component. No $\nu(\text{OH})$ band was observed in the HREEL spectrum. However, a $\nu(\text{OH})$ band was observed on the Au(111) face, indicating that not all of the HCOOH was adsorbed as dimers. Possibly, the HCOOH dissociatively chemisorbed as formate.

Another study³⁰ determined that formic acid had an $E_{\text{ad}} = 13$ kcal/mol, while formaldehyde (HCOH) had $E_{\text{ad}} = 10$ kcal/mol. HCOOH and HCOH both adsorbed molecularly on clean Au(110). In addition, when oxygen adatoms were deposited on the gold surface, the HCOOH reacted with the O adatoms below 210 K to eliminate H_2O and give adsorbed formate. The formate decomposed at 340 K to give off CO_2 , H_2O and HCOOH. Formaldehyde reacted analogously with the O adatoms to give H_2 , H_2O , and adsorbed HCO_2 .

CH₃OH

There has been one report published about the adsorption of methanol on a gold surface.³¹ CH₃OH was adsorbed on the Au(110) face, and its reaction with oxygen adatoms was studied. On the clean gold surface, the adsorptions were weak and molecular, with

$E_{ad} = 12$ kcal/mol. The CH_3OH did react with O adatoms to give H_2O , H_2 , CO_2 , methyl formate (HCOOCH_3), and adsorbed formate. Based on the experimental results, a mechanism for this reaction was proposed:

Note that the O adatom initiates the reaction by abstracting essentially a proton from the methanol; the O adatom is acting as a Brönsted base.

X_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)

Interestingly, there has not been a comprehensive study of halogens adsorbed on gold surfaces. XPS was used by Kishi and Ikeda to look at Cl_2 gas adsorbed on a number of metal films.³² After exposing gold film to Cl_2 , they determined that there were two types of chlorine species that formed on the surface: 1) a Au-Cl species from the dissociation of Cl_2 , and 2) Cl_2 or Cl adsorbed on the Au-Cl species. In 1981, Spencer and Lambert³³ observed surface chloride formation on Au(111). The Cl_2 chemisorbed on the surface at 298 K immediately to give what they proposed as a AuCl_3 surface chloride. There was no observed Cl adsorption overlayer in this case. The authors did state that impurities in the gold sample could have affected the Cl_2 adsorption. In 1986, it was reported that a clean gold film exhibits negligible reactivity with Cl_2 , unlike on silver and copper films where

the Cl_2 readily dissociates and penetrates deeply into the bulk of the metal.³⁴ On the gold film, Cl_2 adsorption to the surface is less than a monolayer at 293 K, and there is no diffusion of Cl or Cl_2 into the bulk of the gold.

One study of Br_2 adsorption on gold has been reported.³⁵ The bromine gas was reported to dissociate on the $\text{Au}(100)$ surface to give 0.5 monolayer coverage. The surface Br formed a typical $c(4 \times 2)R45^\circ$ pattern on the surface, as determined by LEED. At higher pressure, saturation was induced, and the surface coverage increased 10%. This increase was thought to be due to a Br_2 overlayer being formed on the already adsorbed Br atoms.

There is also only one report of I_2 adsorbed on gold.³⁶ The iodine dissociated on $\text{Au}(111)$ to give 0.33 monolayer coverage and form a typical $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern. With an overpressure of I_2 , other incompletely defined surface structures, such as rosettes, were observed, but they reverted back to the previously observed structure once the overpressure was released. All of the I adatoms could be desorbed from the surface as I_2 by heating the sample at 573-773 K. The I_2 adsorption on $\text{Au}(111)$ was observed to be very similar to what the authors observed with $\text{I}_2/\text{Ag}(111)$.³⁷

The adsorption of HF on $\text{Au}(111)$ was mentioned briefly.²⁵ HF adsorbs molecularly with a sticking coefficient close to unity. Multilayer formation does occur. For the monolayer, $E_{\text{ad}} = 7.9$ kcal/mol, and for the multilayer it increases slightly due to intermolecular hydrogen bonding, $E_{\text{ad}} = 8.5$ kcal/mol.

NH₃

- On polycrystalline gold film, ammonia adsorbs molecularly and reversibly,¹¹ with $E_{ad} = 13.6$ kcal/mol. Surface potential measurements of the gold film indicated that the NH₃ may be penetrating into the subsurface region of the film. In a much later study, NH₃ was adsorbed on Au(111).²⁵ The E_{ad} value was indeterminate, but the ammonia did appear to be bonding molecularly through the lone pair on the nitrogen atom. Multilayer formation also occurred at 85 K, most likely due to hydrogen bonding between the molecules.

Nitrogen Oxides

A UHV study of nitrogen oxides on Au(111) was conducted by Bartram and Koel.³⁷ NO and N₂O did not adsorb on Au(111) at 95 K under UHV conditions, but NO₂ did adsorb molecularly to about 0.4 monolayer. The NO₂ forms a O,O'-nitrito chelate with C_{2v} symmetry on the surface.

The vibrational frequencies of $\text{NO}_2/\text{Au}(111)$ correlate well to those in the homogeneous compound $\text{Ni}(\text{picoline})_2(\text{O}_2\text{N})_2$. The adsorption is reversible with $E_{\text{ad}} = 14$ kcal/mol. With high NO_2 exposure, N_2O_4 can be formed on the surface.

When the adsorbed NO_2 was exposed to NO , N_2O_3 formed in an upright configuration on the surface. Here again, the vibrational frequencies of $\text{N}_2\text{O}_3/\text{Au}(111)$ closely match those of N_2O_3 in solution.

C_2H_4 and C_2H_2

There have been a few reported studies on small hydrocarbons adsorbed on gold. Ethylene adsorbed weakly and reversibly on gold film;³⁸ no hydrogenation or dehydrogenation of C_2H_4 occurred. On $\text{Au}(111)$, C_2H_4 did not chemisorb, even at 273 K and higher.¹⁶ It did chemisorb readily on $\text{Pt}(111)$. On the $\text{Au}(110)$ surface, ethylene and

acetylene adsorbed weakly and molecularly,³¹ both with $E_{ad} \sim 10$ kcal/mol. The C_2H_4 and C_2H_2 did not react with oxygen adatoms when they were present on the gold surface; no reactivity was observed under similar conditions on Ag(110) and Cu(110).

CH₃CN and PhCN

The adsorption of acetonitrile and benzonitrile on Au(100) has been extensively studied using LEED, TDS, HREELS, and work function measurements.^{39,40} Both molecules adsorb molecularly and reversibly, and without inducing any surface reconstruction. Multilayers form at low temperature. However, the molecules appear to have different bonding modes. The CH₃CN is oriented preferentially with the nitrogen

atom towards the surface and $E_{ad} = 11$ kcal/mol. The PhCN molecule appears to lie with the phenyl ring flat and parallel to the gold surface, with $E_{ad} = 18$ kcal/mol. The physisorptive bond may be through the

π -electron cloud of the molecules. CH_3CN has one π bond, while PhCN has four π bonds that could interact with the gold surface when lying flat and parallel to it. This proposal would explain the contrasting orientations of CH_3CN on the surface, as well as provide a reason for the higher adsorption energy for PhCN . There is little or no perturbation of the adsorbed molecules, as evidenced by a comparison of the $\nu(\text{CN})$ stretching band of the adsorbate with that of the free nitrile.

	gas	monolayer/Au (100)	multilayer/Au (100)
CH_3CN	2268 cm^{-1}	2271 cm^{-1}	2266 cm^{-1}
PhCN	2242 cm^{-1}	2234 cm^{-1}	2247 cm^{-1}

No explanation for the small and opposing shift in wavenumbers from the adsorptions is put forth by the authors. When the $\text{Au}(100)$ surface is dosed with potassium atoms, the acetonitrile and benzonitrile molecules congregate around the potassium adatoms, with the nitrogen atom of the nitrile molecule closest to the potassium to give surface species like $(\text{CH}_3\text{CN})_n\text{K}$ and $(\text{PhCN})_n\text{K}$.⁴⁰ Apparently, the electropositive potassium atoms are inducing this formation by attracting the partially electronegative end of the nitrile molecules. These types of congregated complexes are observed in the gas phase by mass spectrometry.

**PAPER 1. SYNTHESIS AND PROTONATION OF THE BRIDGING
BENZO[b]THIOPHENE (BT) COMPLEXES
[Cp'(CO)₂Re]($\eta^2:\eta^1$ (S)- μ_2 -BT)[Re(CO)₂Cp"]¹**

ABSTRACT

The bimetallic complexes $[\text{Cp}'(\text{CO})_2\text{Re}](\eta^2:\eta^1(\text{S})-\mu_2\text{-BT})[\text{Re}(\text{CO})_2\text{Cp}'']$, $\text{Cp}'=\text{Cp}''= \eta^5\text{-C}_5\text{H}_5$ or $\text{-C}_5\text{Me}_5$, $\text{BT} = \text{benzo}[\text{b}]\text{thiophene}$, are prepared by reaction of the monometallic complex $\text{Cp}'(\text{CO})_2\text{Re}(\text{BT})$ with a catalytic amount of $\text{CF}_3\text{SO}_3\text{H}$ or in the reaction of $\text{Cp}'(\text{CO})_2\text{Re}(\text{THF})$ with BT . An X-ray structural study of $[\text{Cp}(\text{CO})_2\text{Re}]_2(\eta^2:\eta^1(\text{S})-\mu_2\text{-BT})$ shows that one Re is η^2 -coordinated to the 2,3-olefin of the BT and the other is $\eta^1(\text{S})$ -coordinated to the sulfur. Infrared and NMR data of these bimetallic complexes suggest that this dual metal coordination to BT enhances the binding abilities of both the sulfur and C2-C3 olefin groups to the Re atoms. When these bimetallic complexes are reacted with one equivalent of $\text{CF}_3\text{SO}_3\text{H}$, the complexes protonate exclusively at the Re atom that is $\eta^1(\text{S})$ bonded to the BT. The protonated complexes are fluxional, and this fluxionality can be explained in terms of *cis-trans* isomerization at the protonated metal center. This same type of fluxionality is observed in the protonated complex $[\text{Cp}(\text{CO})_2\text{ReH}(\text{PPh}_3)]\text{O}_3\text{SCF}_3$.

INTRODUCTION

An important aspect of the mechanism of the hydrodesulfurization (HDS) of thiophene compounds is the mode of thiophene coordination on the transition metal catalyst.^{2,3} In our studies of the HDS of benzo[b]thiophene (BT), we recently reported the compounds $\text{Cp}'(\text{CO})_2\text{Re}(\text{BT})$,⁴ ($\text{Cp}' = \text{Cp} = \eta^5\text{-C}_5\text{H}_5$ or $\text{Cp}' = \text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), where the BT coordinates as an equilibrium mixture of $\eta^1(\text{S})$ and $2,3\text{-}\eta^2$ isomers (eq 1). The relative amounts of isomers in these equilibria

can be explained by assuming that the sulfur in the BT is acting as an electron donor to the metal center in the $\eta^1(\text{S})$ isomer, while the olefin is a π -accepting ligand in the $2,3\text{-}\eta^2$ isomer. In an equilibrium solution of **1**, where $\text{Cp}' = \text{Cp}$, the $\eta^1(\text{S})$ coordination mode is favored over $2,3\text{-}\eta^2$ coordination by a ratio of 3:1. When the electron density on the metal is increased by changing Cp' to Cp^* , the Re becomes a poorer acceptor of electron density from sulfur in the $\eta^1(\text{S})$ isomer but is a better π -backbonder to the olefin in the $2,3\text{-}\eta^2$ isomer; thus, $2,3\text{-}\eta^2$ -bonding is

favored by a ratio of 1.1:1.0 in $\text{Cp}^*(\text{CO})_2\text{Re}(\text{BT})$. When the BT in $\text{Cp}'(\text{CO})_2\text{Re}(\text{BT})$ is replaced by 2-MeBT or 3-MeBT, only the $\eta^1(\text{S})$ isomer is observed because 2-MeBT and 3-MeBT are stronger sulfur-donor ligands and the olefin is probably also coordinated more weakly for both steric and electronic reasons. Heteroatom donor ability and olefin π -acceptor ability similarly affect equilibria between $\eta^1(\text{Se})$ and 2,3- η^2 isomers of the selenophene (Sel) complexes $\text{Cp}'(\text{CO})_2\text{Re}(\text{Sel})$.⁵

In the present paper, we use the $\text{Cp}'(\text{CO})_2\text{Re}(\text{BT})$ complexes to prepare the bimetallic compounds $[\text{Cp}'(\text{CO})_2\text{Re}](\eta^2:\eta^1(\text{S})-\mu_2\text{-BT})[\text{Re}(\text{CO})_2\text{Cp}'']$, in which one Re is bonded to the sulfur and the other is coordinated to the 2,3-olefin of the BT ligand. An X-ray structural determination of $[\text{Cp}(\text{CO})_2\text{Re}]_2(\eta^2:\eta^1(\text{S})-\mu_2\text{-BT})$ is presented. Protonation of these complexes is discussed and explained in terms of the electron-donor and electron-acceptor abilities of the BT and the metal.

EXPERIMENTAL

General Procedures. All reactions were performed under a nitrogen atmosphere in reagent grade solvents using standard Schlenk techniques.⁶ Hexane and CH₂Cl₂ were distilled under nitrogen from CaH₂; tetrahydrofuran (THF) and diethyl ether were distilled from Na/benzophenone. Triflic acid, CF₃SO₃H, was distilled under argon. The NMR spectra were obtained on Nicolet NT-300 or Varian VXR-300 spectrometers using deuterated solvent as an internal lock and internal reference (CD₂Cl₂: δ 5.32 for ¹H and δ 53.8 for ¹³C). Variable temperature NMR spectra were recorded on the Varian instrument. Electron-ionization mass spectra were run on a Finnigan 4000 spectrometer. Infrared spectra of the compounds were recorded in CH₂Cl₂ solution with a Nicolet 710 FT-IR spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN or Desert Analytics, Tuscon, AZ.

The following compounds were prepared by literature methods: 2-MeBT,⁷ Cp*Re(CO)₃,⁸ CpRe(CO)₃,⁹ Cp(CO)₂Re(PPh₃)¹⁰ (**4**), Cp*(CO)₂Re(PPh₃).¹⁰ Infrared, ¹H NMR, and ¹³C NMR data are tabulated in Tables I, II, and III, respectively, at the end of the Experimental section.

Cp(CO)₂Re(η ¹(S)-BT) (**1a**) and Cp(CO)₂Re(2.3- η ²-BT) (**1b**).

Compound **1** was prepared by a modified version of the reported synthesis.⁴ A solution of Cp(CO)₂Re(THF),¹¹ prepared by UV irradiation of a THF solution (20 mL) of CpRe(CO)₃ (0.20 g, 0.60 mmol) at -16 °C, was stirred with BT (0.25 g, 1.9 mmol) and 6 mL of hexanes¹² at room

temperature for 12 h. The solvent was then removed under vacuum, and the residue was chromatographed on a neutral alumina (5% w/w H₂O) column (1 cm x 15 cm). Unreacted CpRe(CO)₃ was eluted with hexanes, and then a yellow band containing the product was eluted with hexanes-CH₂Cl₂ (4:1). Slow evaporation of the solvent under vacuum from the yellow eluent at 0 °C gave a moderately air-stable yellow powder of **1** (0.097 g, 38%), which was characterized by its infrared, ¹H NMR and ¹³C NMR spectra (Tables I-III) by comparison with previously reported data.⁴

Cp*(CO)₂Re(η¹(S)-BT) (**2a**) and Cp*(CO)₂Re(2.3-η²-BT) (**2b**).

Compound **2** was prepared in a similar manner as that described for **1** starting with Cp*Re(CO)₃ (0.20 g, 0.49 mmol) and BT (0.25 g, 1.9 mmol). Product **2** was isolated as a moderately air-stable yellow powder (0.079 g, 31%).⁴

Cp(CO)₂Re(2-MeBT) (**3**). Compound **3** was synthesized analogously to compound **1**. Only the η¹(S)- form of the compound was formed; product **3** was isolated as a moderately air stable yellow powder (0.79 g, 29%).⁴

[Cp(CO)₂Re]₂(η²:η¹(S)-μ₂-BT) (**5**). This compound was prepared by first dissolving **1** (0.020 g, 0.045 mmol) in ~1 mL of CH₂Cl₂ in a 25 mL Schlenk flask to give a clear yellow solution. Then, a catalytic amount of CF₃SO₃H (0.1 mL, 0.001 mmol) was added and the solution was stirred, whereupon the color immediately turned a clear brown. When the reaction is carried out in CD₂Cl₂, a ¹H NMR spectrum of the solution at -60 °C showed near quantitative conversion to **5**. Compound **5** was

isolated as a brown solid (0.011 g, 67%) by precipitation from the solution with hexanes at 0 °C. EIMS (70 eV) m/e 750 (M^+ based on ^{187}Re). Anal. calcd. for $\text{C}_{22}\text{H}_{16}\text{O}_4\text{Re}_2\text{S}$: C, 35.28; H, 2.15. Found: C, 34.70; H, 2.10.

Compound **5** was also isolated in less than 5% yield from the synthesis of **1**. After eluting **1** from the alumina column, compound **5** was eluted as a clear light tan band using 3:2 hexanes- CH_2Cl_2 . It is helpful to follow the progress of the elution with FT-IR since the intensity of the tan color is very weak.

$[\text{Cp}^*(\text{CO})_2\text{Re}]_2(\eta^2:\eta^1(\text{S})-\mu_2\text{-BT})$ (**6**). This compound was synthesized following the procedure for **5**. Compound **2** (0.025 g, 0.049 mmol) and a catalytic amount of $\text{CF}_3\text{SO}_3\text{H}$ (0.1 mL, 0.001 mmol) were reacted in 0.55 mL of CD_2Cl_2 ; a ^1H NMR spectrum of the solution at 20 °C showed near quantitative conversion to **6**. Compound **6** was isolated as a brown solid (0.017g, 78%) in the same manner as **5**. Compound **6** was also isolated in less than 5% yield from the synthesis of **2** in the same way that **5** was isolated from the synthesis of **1**. Anal. calcd. for $\text{C}_{32}\text{H}_{36}\text{O}_4\text{Re}_2\text{S}$: C, 43.23; H, 4.28. Found: C, 42.50; H, 3.94.

$[\text{Cp}(\text{CO})_2\text{Re}](\eta^2:\eta^1(\text{S})-\mu_2\text{-BT})[\text{Re}(\text{CO})_2\text{Cp}^*]$ (**7**). This compound was synthesized in a manner similar to that for **1**. A THF solution of $\text{Cp}(\text{CO})_2\text{Re}(\text{THF})$, formed by UV-irradiation of $\text{CpRe}(\text{CO})_3$ (0.20 g, 0.060 mmol), was stirred with **2** (0.060 g, 0.012 mmol) and 6 mL of hexanes for 12 h. The solvent was then removed under vacuum, and the residue was chromatographed as for **1**. After eluting unreacted $\text{CpRe}(\text{CO})_3$ with hexanes and unreacted **2** with 4:1 hexanes- CH_2Cl_2 , compound **7** was

eluted with 3:2 hexanes-CH₂Cl₂ as a clear tan solution. Solvent was then removed from the product band under vacuum, and the residue was dissolved in 2 mL of CH₂Cl₂ and cooled to 0 °C. Addition of 40 mL of hexanes precipitated **7** as an air-stable, light cream-colored solid (0.038 g, 40% based on **2**). Anal. calcd. for C₂₇H₂₆O₄Re₂S; C, 39.60; H, 3.20. Found: C, 40.01, H, 2.99.

Protonation of complexes **1**, **2**, **7** and **3** to give complexes **8**, **9**, **10** and **11**, respectively. General procedure. These compounds were prepared in a manner similar to **5**, but a stoichiometric amount of CF₃SO₃H was used. For compound **8**, compound **1** (0.020 g, 0.045 mmol) and CF₃SO₃H (2.0 mL, 0.023 mmol) were reacted in 0.55 mL of CD₂Cl₂ (CH₂Cl₂ can also be used) in a 5 mm NMR tube. A ¹H NMR spectrum of the solution at -60 °C showed complete conversion to {[Cp(CO)₂Re(H)](η²:η¹(S)-μ₂-BT)[Re(CO)₂Cp]}O₃SCF₃ (**8**). Compound **8** was isolated as a brown solid by precipitation from the solution with diethyl ether at 0 °C. Complexes **9**, **10**, and **11** were prepared in the same way.

These protonated compounds were insufficiently stable to give satisfactory elemental analyses. Attempts to grow crystals for X-ray structural determination were also unsuccessful. Therefore, they were characterized on the basis of their spectral data, as discussed in the Results and Discussion section.

Reaction of **2** with PPh₃ and CF₃SO₃H. Compound **2** (0.010 g, 0.020 mmol) and PPh₃ (0.1005 g, 0.020 mmol) were dissolved in 0.55 mL of CD₂Cl₂ in a 5 mm NMR tube. The ¹H and ³¹P spectra of the solution

were recorded after 30 minutes at ambient temperature and showed only pure **2** and PPh₃. Then CF₃SO₃H (0.1 mL, 0.001 mmol) was added, and the NMR tube was shaken. There was no apparent change in color. However, after several minutes, the ¹H and ³¹P NMR spectra showed that neither **2** nor **6** were present. The major product was Cp*(CO)₂Re(PPh₃), which was confirmed by comparison of the ¹H and ³¹P NMR spectra with those of the pure compound.

[Cp(CO)₂(H)Re(PPh₃)](CF₃SO₃) (**12**). Compound **12** was synthesized in a 0.55 mL CD₂Cl₂ solution in a 5 mm NMR tube by reaction of Cp(CO)₂Re(PPh₃) (**4**) (0.075 g, 0.13 mmol) with CF₃SO₃H (11.7 mL, 0.132 mmol). A ¹H NMR spectrum of the solution at ambient temperature showed considerable broadening of the signals. However, upon cooling the solution to -60 °C, the spectrum showed the previously reported¹³ **12** present as both the *cis* (**12a**) and *trans* (**12b**) forms, as well as some unprotonated Cp(CO)₂Re(PPh₃) (**4**).

X-ray Structure Determination of **5**. A single crystal of **5** suitable for X-ray diffraction study was obtained by slow diffusion of hexanes into a CH₂Cl₂ solution of **5** at -20 °C. The brown cube-shaped crystals tended to grow in complex twin formations, so the crystal used for data collection was cut from one of these formations. Data collection and reduction parameters are given in Table IV. The structure was solved using a combination of direct methods¹⁴ and a local Fourier program. The non-hydrogen, non-carbon atoms were refined anisotropically. The carbon atoms constrained by the aromatic thiophenic ring were also refined anisotropically. The carbon atoms of

the cyclopentadienyl rings and the carbonyl ligands were refined isotropically. These carbons showed effects which could be attributable to slight disorder and/or large thermal motion; they could not be adequately refined anisotropically and somewhat degraded the refinement of the other lighter atoms. Neutral atom scattering factors were taken from Cromer and Waber.¹⁵ Anomalous dispersion effects were included in F_{calc} ;¹⁶ the values of $\Delta f'$ and $\Delta f''$ were those of Cromer.¹⁷ All direct methods calculations were performed using the TEXSAN crystallographic software package.¹⁸ The Fourier calculations were made using FOUR.¹⁹ Selected bond distances and angles are given in Tables V and VI, respectively. Figure 1 shows an ORTEP drawing of $[\text{Cp}(\text{CO})_2\text{Re}]_2(\eta^2:\eta^1(\text{S})-\mu_2\text{-BT})$ (**5**).

Table I. FTIR Data, $\nu(\text{CO})$ cm^{-1} for the Compounds in CH_2Cl_2 .

compound formula		bands
1 a	$\text{Cp}(\text{CO})_2\text{Re}(\eta^1(\text{S})\text{-BT})$	1940 (s), 1870 (s)
1 b	$\text{Cp}(\text{CO})_2\text{Re}(2,3\text{-}\eta^2\text{-BT})$	1975 (s), 1910 (s)
2 a	$\text{Cp}^*(\text{CO})_2\text{Re}(\eta^1(\text{S})\text{-BT})$	1914 (s), 1844 (s)
2 b	$\text{Cp}^*(\text{CO})_2\text{Re}(2,3\text{-}\eta^2\text{-BT})$	1957 (s), 1885 (s)
3	$\text{Cp}(\text{CO})_2\text{Re}(\eta^1(\text{S})\text{-2-MeBT})$	1929 (s), 1870 (s)
4	$\text{Cp}(\text{CO})_2\text{Re}(\text{PPh}_3)$	1944 (s), 1880 (s)
5	$[\text{Cp}(\text{CO})_2\text{Re}]_2(\eta^2:\eta^1(\text{S})\text{-}\mu_2\text{-BT})$	1984 (s), 1921 (vs,br), 1850 (s)
6	$[\text{Cp}^*(\text{CO})_2\text{Re}]_2(\eta^2:\eta^1(\text{S})\text{-}\mu_2\text{-BT})$	1966 (s), 1904 (s), 1892 (s), 1835 (s)
7	$[\text{Cp}(\text{CO})_2\text{Re}](\eta^2:\eta^1(\text{S})\text{-}\mu_2\text{-BT})[\text{Re}(\text{CO})_2\text{Cp}^*]$	1971 (s), 1919 (s), 1897 (s), 1848 (s)
8	$(5\text{H}^+)(\text{O}_3\text{SCF}_3^-)$	2053 (s), 1990 (vs,br), 1919 (s)
9	$(6\text{H}^+)(\text{O}_3\text{SCF}_3^-)$	2037 (s), 1983 (s), 1971 (s), 1912 (s)
1 0	$(7\text{H}^+)(\text{O}_3\text{SCF}_3^-)$	2050 (s), 1980 (vs,br), 1920 (s)
1 1	$(3\text{H}^+)(\text{O}_3\text{SCF}_3^-)$	2040 (s), 1970 (s)
1 2 a	$[\text{cis-Cp}(\text{CO})_2\text{HRe}(\text{PPh}_3)]\text{O}_3\text{SCF}_3$	2037 (s), 1967 (s)
1 2 b	$[\text{trans-Cp}(\text{CO})_2\text{HRe}(\text{PPh}_3)]\text{O}_3\text{SCF}_3$	(not observed)

Table II. ^1H NMR Data (δ) for the Complexes in CD_2Cl_2 .

Complex	BT	Cp or Cp*	Me on BT	Re-H
1 a	7.88-7.43 (3 m, 4H), 7.28 (d, 1H) ^{a,o} 7.16 (d, 1H) ^{a,o}	4.85 (s, 5H)		
1 b	7.67 (d, 1H) ^b , 7.33 (d, 1H) ^b , 7.19 (t of d, 1H) ^{b,c} 7.10 (t of d, 1H) ^{b,c} , 5.36 (d, 1H) ^{d,o} , 5.12 (d, 1H) ^{d,o}	5.08 (s, 5H)		
2 a	7.77-7.11 (3 m, 6H)	1.81 (s, 15H)		
2 b	7.54 (d, 1H) ^e , 7.28 (d, 1H) ^e , 7.13 (t of d, 1H) ^{e,c} , 7.03 (t of d, 1H) ^{e,c} , 4.27 (d, 1H) ^{f,o} , 3.97 (d, 1H) ^{f,o}	2.02 (s, 15H)		
3	7.76 (d of d, 1H) ^{g,h} , 7.58 (d of d, 1H) ^{g,h} , 7.36 (m, 2H), 7.04 (s, 1H)	4.83 (s, 5H)	2.41 (d, 3H) ⁱ	
4 j		5.05 (s, 5H)		
5	7.51 (d, 1H) ^b , 7.34 (d, 1H) ^b , 7.25 (t of d, 1H) ^{b,c} , 7.15 (t of d, 1H) ^{b,c} , 4.93 (d, 1H) ^{d,o} , 4.67 (d, 1H) ^{d,o}	5.24 (s, 5H), 4.93 (s, 5H)		

Table II (continued)

6	7.43 (d, 1H) ^e , 7.18 (m, 2H), 7.10 (t of d) ^{e,c} , 3.92 (d, 1H) ^{f,o} , 3.68 (d, 1H) ^{f,o}	2.05 (s, 15H), 2.02 (s, 15H)	
7	7.44 (d, 1H) ^b , 7.25 (d, 1H) ^b , 7.22 (t of d, 1H) ^{b,c} , 7.09 (t of d, 1H) ^{b,c} , 3.94 (d, 1H) ^{d,o} , 3.66 (d, 1H) ^{d,o}	4.93 (s, 5H), 2.03 (s, 15H)	
8^m	7.64-7.25 (3 m, 4H), 5.52 (d, 1H) ^{d,o} , 4.84 (d, 1H) ^{d,o}	5.57 (s, 5H), 5.55 (s, 5H)	-8.67 (s)
9^m	7.54-7.19 (3 m, 4H), 3.98 (d, 1H) ^{d,o} , 3.64 (d, 1H) ^{d,o}	2.32 (s, 15H), 2.05 (s, 15H)	-8.38 (s)
10^m	7.56-7.23 (4 m, 4H), 4.09 (d, 1H) ^{d,o} , 3.79 (d, 1H) ^{d,o}	5.49 (s, 5H), 2.06 (s, 15H)	-8.60 (s)
11	7.78-7.48 (3 m, 4H), 7.19 (s, 1H)	5.18 (s)	2.46 (d) ⁱ -7.87 (s)
12a^{m,n}		5.72 (s)	-7.83 (d) ^k
12b^{m,n}		5.53 (s)	-8.86 (d) ^l

^{a1}J_{H2-H3} = 5.4 Hz. ^{b1}J = 7.8 Hz. ^{c2}J = 1.2 Hz. ^{d1}J_{H2-H3} = 6.0 Hz. ^{e1}J = 7.5 Hz. ^{f1}J_{H2-H3} = 6.3 Hz.

^{g1}J = 6.0 Hz. ^{h2}J = 1.8 Hz. ⁱ²J_{H3-CH3} = 1.2 Hz. ^jPPh₃ = 7.40 (m, 18H). ^{k1}J_{PH} = 41.7 Hz.

^{l1}J_{PH} = 14.7 Hz. ^mAt -60 °C. ⁿPPh₃ is a broad multiplet. ^oH₂ or H₃ resonance.

Table III. ^{13}C NMR Data (δ) for the complexes in CD_2Cl_2 .

Complex	BT ^a	Cp or Cp [*]	Me on Cp [*]	CO
1	145.6, 144.4, 139.1, 139.0, 126.6, 126.4, 125.6, 124.1, 123.9, 123.6, 123.3, 122.2, 56.2 ⁱ , 34.2 ⁱ	88.0, 83.8		203.3, 202.5, 200.1
2	145.6, 137.8, 128.1, 126.7, 125.5, 124.6, 123.7, 123.4, 123.2, 122.6, 47.9 ⁱ , 46.6 ⁱ	97.8, 95.9	10.2, 10.4	204.4, 204.3, 205.5
3^b	152.4, 151.3, 139.7, 127.6, 125.5, 124.4, 124.2, 124.1	83.7		202.2
4^c		84.2		202.8 (d) ^d
5	147.3, 145.5, 127.5, 127.0, 126.0, 124.8, 56.3 ⁱ , 36.1 ⁱ	88.8, 83.8		203.2, 203.0, 202.0, 200.2
6	147.5, 142.7, 126.7, 126.1, 125.6, 124.6, 60.9 ⁱ , 42.3 ⁱ	99.1, 95.9	10.9, 10.3	207.6, 206.7, 204.5, 204.1
7	147.8, 144.9, 127.0, 126.4, 126.0, 124.0, 61.7 ⁱ , 41.1 ⁱ	99.2, 83.6	10.3	204.8, 203.6, 203.3, 203.0

Table III (continued)

8^e	148.0, 135.2, 129.0, 127.6, 125.6, 125.1, 46.0 ⁱ , 32.0 ⁱ	89.3, 88.5	201.8, 199.4, 189.9, 188.9
9^e	149.7, 131.4, 129.8, 127.1, 126.1, 125.3, 50.3 ⁱ , 38.7 ⁱ	102.9, 100.4	204.0, 203.3, 194.1, 192.6
10^e	146.8, 143.9, 126.4, 126.3, 125.8, 123.4, 60.3 ⁱ , 40.0 ⁱ	98.6, 83.7	206.1, 203.6, 203.5, 203.2
11	141-124	86.7	
12a^e		90.0	196.0 (d) ^f , 190.6 (d) ^g
12b^e		89.1	189.5 (d) ^h

^aSome overlap of resonances occurs. ^bMeBT at 14.7. ^cPPh₃ at 138.4 (d), 133.4 (d), 130.0 (d),

128.4 (d). ^dJ_{PC} = 8.6 Hz. ^eAt -60 °C. ^fJ_{PC(cis)} = 19.5 Hz. ^gJ_{PC(trans)} = 5.4 Hz. ^hJ_{PC(cis)} = 17.7 Hz.

ⁱC2 or C3.

Table IV. Crystal and Data Collection Parameters for
 $[\text{Cp}(\text{CO})_2\text{Re}]_2(\eta^2:\eta^1(\text{S})-\mu_2\text{-BT})$ (**5**).

A. Crystal Data	
Empirical Formula	$[\text{Re}(\text{CO})_2(\text{C}_5\text{H}_5)]_2(\text{SC}_8\text{H}_6)$
Formula Weight	746.82
Lattice Parameters:	
a	12.265 (7) Å
b	11.162 (6) Å
c	15.816 (5) Å
β	109.28 (3)°
V	2044 (2) Å ³
Space Group	P2 ₁ /c (#14)
Z value	4
D _{calc}	2.427 g/cm ³
$\mu(\text{MoK}\alpha)$	121.20 cm ⁻¹
B. Intensity Measurements	
Diffractometer	Rigaku AFC6R
Radiation	MoK α (λ = 0.71069 Å)
Temperature	23 °C
Scan Type	ω -2 θ
Scan Rate	16.0°/min (in omega) (2 rescans)
No. of Reflections Measured	Total: 4024 Unique: 3837 (R_{int} = .103)

Table IV (continued)

Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.60-1.00)

C. Structure Solution and Refinement

Function Minimized	$\Sigma w(F_o - F_c)^2$
Least-squares Weights	$4F_o^2/\sigma^2(F_o^2)$
p-factor	0.03
Anomalous Dispersion	All non-hydrogen atoms
Residuals: R; R _w	0.044; 0.046
Goodness of Fit Indicator	1.36
Max Shift/Error in Final Cycle	0.40
Maximum Peak in Final Diff. Map	1.35 e ⁻ /Å ³
Minimum Peak in Final Diff. Map	-1.38 e ⁻ /Å ³

Table V. Selected Intramolecular Distances (Å) for
 $[\text{Cp}(\text{CO})_2\text{Re}]_2(\eta^2:\eta^1(\text{S})-\mu_2\text{-BT})$ (5).^a

bond	distance	bond	distance
RE1-S	2.35 (1)	O2AA-C2AA	1.16 (4)
RE1-C1AA	1.84 (4)	O2BB-C2BB	1.12 (4)
RE1-C1BB	1.83 (4)	C2-C3	1.35 (5)
RE2-C2AA	1.90 (4)	C3-C8	1.42 (5)
RE2-C2BB	1.85 (4)	C8-C9	1.44 (4)
RE2-C2	2.17 (3)	C8-C4	1.41 (5)
RE2-C3	2.22 (3)	C9-C7	1.40 (4)
S-C2	1.81 (3)	C7-C6	1.36 (4)
S-C9	1.77 (3)	C6-C5	1.34 (6)
O1AA-C1AA	1.23 (4)	C5-C4	1.31 (5)
O1BB-C1BB	1.17 (4)		

^aEstimated standard deviations in the least significant figure are given in parentheses.

Table VI. Selected Intramolecular Bond Angles (deg) for
 $[\text{Cp}(\text{CO})_2\text{Re}]_2(\eta^2:\eta^1(\text{S})-\mu_2\text{-BT})$ (5).^a

bonds	angle (°)	bonds	angle(°)
S-RE1-C1AA	93 (1)	C3-RE2-C2BB	110 (1)
S--RE1-C1BB	91 (1)	C2AA-RE2- C2BB	88 (2)
C1AA-RE1-C1BB	88 (2)	RE1-C1BB- O1BB	172 (3)
RE1-S-C2	114 (1)	RE2-C3-C2	71 (2)
RE1-S-C9	107 (1)	RE2-C3-C8	121 (2)
C2-S-C9	90 (2)	C3-C8-C9	115 (3)
RE2-C2-S	124 (1)	C3-C8-C4	136 (3)
RE2-C2-C3	74 (2)	C9-C8-C4	109 (3)
S-C2-C3	114 (3)	S-C9-C8	109 (3)
RE1-C1AA-O1AA	177 (4)	S-C9-C7	127 (3)
C2-C3-C8	112 (3)	C8-C9-C7	124 (3)
RE2-C2AA-O2AA	176 (3)	C9-C7-C6	118 (4)
RE2-C2BB-O2BB	173 (3)	C7-C6-C5	121 (4)
C2-RE2-C2AA	110 (1)	C6-C5-C4	121 (4)
C2-RE2-C2BB	88 (1)	C8-C4-C5	127 (3)

^aEstimated standard deviations in the least significant figure are given in parentheses.

RESULTS AND DISCUSSION

Synthesis of $\text{Cp}'(\text{CO})_2\text{Re}(\text{BT})$ (**1** and **2**) and $[\text{Cp}'(\text{CO})_2\text{Re}]_2(\eta^2:\eta^1(\text{S})-\mu_2\text{-BT})$ (**5** and **6**) Complexes. The reaction of $\text{Cp}(\text{CO})_2\text{Re}(\text{THF})$ with benzo[*b*]thiophene in THF solution results (eq 2) in the formation of the monometallic compound $\text{Cp}(\text{CO})_2\text{Re}(\text{BT})$ (**1**)⁴ discussed in the Introduction and a small amount (~5% yield) of the bimetallic compound $[\text{Cp}(\text{CO})_2\text{Re}]_2(\eta^2:\eta^1(\text{S})-\mu_2\text{-BT})$ (**5**). Compound **1** consists (eq 1) of two

isomers, $\eta^1(\text{S})$ (**1a**) and $2,3-\eta^2$ (**1b**).⁴ The ^1H NMR spectrum of **1b** (Table II) shows that the H2 and H3 resonances (δ 5.36 and 5.12) are substantially upfield compared to those in free BT (δ 7.33 (H2) and 7.22 (H3)).²⁰ In the ^{13}C NMR spectrum (Table III) of **1b**, two of the ^{13}C NMR resonances (δ 56.2 and 34.2), presumably those of C2 and C3, are also substantially upfield of those (δ 126.2 (C2) and 123.8 (C3)) in free BT.²¹ The ^1H and ^{13}C NMR spectra of the bimetallic compound **5** show

that the H2 and H3 resonances (δ 4.93 and 4.67) and C2 and C3 resonances (δ 56.3 and 36.1) are very similar to those in the 2,3- η^2 isomer **1b** (see Tables II and III). The X-ray structure determination of **5** (to be discussed in detail later) shows that one Re atom is coordinated to C2 and C3 of the BT above the BT plane and confirms the 2,3- η^2 assignment. The X-ray structure determination also confirms that a $\text{Cp}(\text{CO})_2\text{Re}$ fragment is $\eta^1(\text{S})$ bonded to the BT.

The ^1H NMR chemical shifts for the Cp ligands in **5** (δ 5.24 and 4.93) can be assigned by comparison with spectra of isomers **1a** and **1b**. The chemical shift for the Cp in the $\eta^1(\text{S})$ isomer of **1a** (δ 4.85) is upfield of the resonance for the 2,3- η^2 isomer **1b** (δ 5.08). Similarly, in **5**, the upfield resonance at δ 4.93 can be assigned to the Cp on the Re atom that is $\eta^1(\text{S})$ bonded to the BT, while the resonance at δ 5.24 may be attributed to the Cp on the Re atom that is 2,3- η^2 bonded to the BT.

In the infrared spectra, $\nu(\text{CO})$ values (Table I) of the $\eta^1(\text{S})$ isomer **1a** occur at 1940, 1870 cm^{-1} while those of the 2,3- η^2 isomer **1b** are at 1975, 1910 cm^{-1} . Thus, 2,3- η^2 BT coordination gives $\nu(\text{CO})$ values that are about 35-40 cm^{-1} higher than those in the complex in which the BT is S-coordinated.⁴ Thus, the $\nu(\text{CO})$ bands at 1984 and 1921 cm^{-1} in **5** can be assigned to the 2,3- η^2 coordinated $\text{Re}(\text{CO})_2\text{Cp}$ and those at 1921 and 1850 cm^{-1} are assigned to the S-coordinated $\text{Re}(\text{CO})_2\text{Cp}$ group.

The $\nu(\text{CO})$ values for the carbonyls on the Re that is S-bonded in **5** are about 20 cm^{-1} lower than the corresponding values in **1a**. This result suggests that the sulfur in **5** provides more electron density to

the metal, thereby increasing π back-bonding from the metal to the CO π^* orbitals. This increased back-bonding weakens the CO bond, which lowers the $\nu(\text{CO})$ values in **5** as compared to **1a**. Thus, the $\nu(\text{CO})$ values indicate that the sulfur of the BT in **5** is more strongly electron-donating to the Re atom than the BT is in the S-bonded monometallic compound **1a**. On the other hand, the $\nu(\text{CO})$ values for the carbonyls on the Re that is 2,3- η^2 bonded to the BT are about 10 cm^{-1} higher than the corresponding values in **1b**. This indicates that in **5** there is increased π back-bonding from the Re to the 2,3- η^2 olefinic bond of the BT, resulting in less electron density on the Re which increases the $\nu(\text{CO})$ values. Thus, in **5** the Re-olefin bond is strengthened by increased π back-bonding and the Re-S bond is strengthened by enhanced sulfur donation as compared with the monometallic complexes **1a** and **1b**. This flow of electron density from the 2,3- η^2 -coordinated Re to the S-coordinated Re is supported by ^1H NMR data for the H2 and H3 atoms in the compounds. In **5**, the H2 and H3 NMR resonances (δ 4.93 (d) and 4.67 (d)) are considerably upfield of those in **1b** (δ 5.36 (d) and 5.12 (d)).

The Cp^* analogs of **1** and **5** were prepared in the same manner (eq 2) as for **1** from the reaction of $\text{Cp}^*(\text{CO})_2\text{Re}(\text{THF})$ with BT. Compound **2** also exists in solution as an equilibrium mixture of $\eta^1(\text{S})$ (**2a**) and 2,3- η^2 (**2b**) isomers (eq 1). The bimetallic compound **6** is also formed in the reaction. As for **5**, the FT-IR and ^1H NMR spectroscopic data show that in **6**, the sulfur of the BT is more strongly electron-donating than in the monometallic compound **2a**, and the 2,3-olefin is more π -

accepting than in the monometallic compound **2b**. In **6**, the $\nu(\text{CO})$ bands for the η^2 bonded metal fragment (1966 and 1892 cm^{-1}) are 7-8 cm^{-1} higher than those in the η^2 isomer **2b** (1957 and 1885 cm^{-1}), while the carbonyl bands for the S-bonded metal fragment in **6** (1904 and 1835 cm^{-1}) are 9-10 cm^{-1} lower than those in the $\eta^1(\text{S})$ isomer **2a** (1914 and 1844 cm^{-1}). Also, in the ^1H NMR spectra, the H2 and H3 resonances in bimetallic **6** (δ 3.92 (d), 3.68 (d)) are ~ 0.3 ppm upfield of those in monometallic **2b** (δ 4.27 (d), 3.97 (d)).

Compound **7**, the bimetallic compound containing one $\text{Cp}(\text{CO})_2\text{Re}$ fragment and one $\text{Cp}^*(\text{CO})_2\text{Re}$ fragment is synthesized (eq 3) from the reaction of $\text{Cp}(\text{CO})_2\text{Re}(\text{THF})$ with **2**. In **7**, the $\text{Cp}(\text{CO})_2\text{Re}$ fragment is exclusively $\eta^1(\text{S})$ bonded to the BT, and the $\text{Cp}^*(\text{CO})_2\text{Re}$ fragment is exclusively 2,3- η^2 bonded to the BT. This bonding assignment is based

on ^1H NMR and FTIR data. In the ^1H NMR spectrum the Cp resonance for **7** (δ 4.93) is identical to the position of the more upfield Cp resonance of the S-bonded $\text{Cp}(\text{CO})_2\text{Re}$ fragment in **5**, which strongly supports S-

coordination by the $\text{Cp}(\text{CO})_2\text{Re}$ group in **7**. In addition, the H2 and H3 atoms (δ 3.94 and 3.66) are shifted upfield of those in the Cp-containing bimetallic compound **5** (δ 4.93 and 4.67) but closely match those in the Cp^* -containing bimetallic compound **6** (δ 3.92 and 3.68). In the FTIR spectrum of **7**, the $\nu(\text{CO})$ values for the CO groups on the S-bonded $\text{Cp}(\text{CO})_2\text{Re}$ fragment (1919 and 1848 cm^{-1}) are nearly the same as those for the S-bonded $\text{Cp}(\text{CO})_2\text{Re}$ fragment in **5** (1921 and 1850 cm^{-1}). In addition, the bands for the $\text{Cp}^*(\text{CO})_2\text{Re}$ fragment in **7** (1971 and 1897 cm^{-1}) closely match those for the 2,3- η^2 bonded $\text{Cp}^*(\text{CO})_2\text{Re}$ fragment in **6** (1966 and 1892 cm^{-1}). The only detected isomer of **7** is that in which the $\text{Cp}(\text{CO})_2\text{Re}$ is bonded to the BT sulfur and the $\text{Cp}^*(\text{CO})_2\text{Re}$ is bonded to the olefin. There was no evidence for the isomer in which the $\text{Cp}(\text{CO})_2\text{Re}$ and $\text{Cp}^*(\text{CO})_2\text{Re}$ fragments are interchanged. Such an isomer would be expected to be less stable because the Cp^* ligand would make the $\text{Cp}^*(\text{CO})_2\text{Re}$ fragment less Lewis acidic for binding to the electron-donating sulfur. At the same time, the less electron-rich $\text{Cp}(\text{CO})_2\text{Re}$ fragment would be less capable of π back-bonding to the olefinic group.

Reactions of $\text{Cp}'(\text{CO})_2\text{Re}(\text{BT})$ Complexes with $\text{CF}_3\text{SO}_3\text{H}$. When one equivalent of $\text{Cp}'(\text{CO})_2\text{Re}(\text{BT})$ is reacted with one half an equivalent or greater of $\text{CF}_3\text{SO}_3\text{H}$, the protonated bimetallic complex $[\text{Cp}'(\text{CO})_2\text{ReH}](\eta^2:\eta^1(\text{S})-\mu_2\text{-BT})[\text{Re}(\text{CO})_2\text{Cp}']$ is formed immediately (Scheme I). If the $\text{Cp}'(\text{CO})_2\text{Re}(\text{BT})$ complex is reacted with less than half an equivalent of $\text{CF}_3\text{SO}_3\text{H}$, a mixture of the protonated bimetallic complex and the unprotonated bimetallic complex

$[\text{Cp}'(\text{CO})_2\text{Re}]_2(\eta^2:\eta^1(\text{S})-\mu_2\text{-BT})$ is immediately formed. The bimetallic compounds **5** and **6** are synthesized in quantitative yield by the reaction of **1** and **2**, respectively, with catalytic amounts (1:40) of $\text{CF}_3\text{SO}_3\text{H}$ (Scheme I). Thus, this acid-catalyzed method is far superior to the reaction in eq 2 for the syntheses of **5** and **6**.

Scheme I

The protonated bimetallic complex **8** can also be synthesized (eq 4) by reaction of the bimetallic complex **5** with one equivalent of acid; **9** can be synthesized from **6** in the same manner. Compound **7** also reacts (eq 4) with one equivalent of $\text{CF}_3\text{SO}_3\text{H}$ to give **10** (eq 4). The protonated complexes **8**, **9** and **10** are all fluxional (*vide infra*) at room temperature in solution as indicated by the broad peaks in their ^1H and ^{13}C NMR spectra. However, the fluxionality can be frozen out by cooling

solutions of the compounds to $-60\text{ }^\circ\text{C}$, and good quality NMR spectra can be obtained at this temperature. Compounds **5**, **6** and **7** are protonated exclusively at the Re that is S-bonded to the BT to give **8**, **9** and **10**, respectively. Evidence for this site of protonation is seen in a comparison of the ^1H NMR Cp and Cp* resonances of **7** and **10** (Table II). In **7**, the $\text{Cp}(\text{CO})_2\text{Re}$ fragment is S-bonded to the BT, while the $\text{Cp}^*(\text{CO})_2\text{Re}$ fragment is 2,3- η^2 bonded (*vide supra*). Upon protonation of **7**, the Cp resonance shifts downfield from 4.93 ppm to 5.49 ppm, while the Cp* resonance shifts only very slightly downfield from 2.03 to 2.06 ppm. This indicates that the S-coordinated $\text{Cp}(\text{CO})_2\text{Re}$ unit is protonated, despite the fact that the Cp* ligand is more electron-donating than Cp. However, protonation at the S-coordinated Re would strengthen the sulfur-Re donor bond as well as the π -bond from Re to

the olefin; these factors are apparently responsible for the observed protonation at the $\text{Cp}(\text{CO})_2\text{Re}$ group. The Cp resonances (4.93 and 5.24 ppm) of **5** shift to 5.55 and 5.57 ppm upon protonation to give **8**. The Cp^* resonances of **6** shift from 2.02 and 2.05 ppm to 2.05 and 2.32 upon protonation to give **9**. These downfield shifts of one Cp or Cp^* resonance are consistent with the idea that the $\text{Cp}'(\text{CO})_2\text{Re}$ fragment that is S-bonded to the BT is protonated.

Only one hydride resonance is observed in the ^1H NMR spectra (Table II) of the protonated bimetallic complexes; so, only one metal center is protonated. The protonated bimetallic complexes are stable in an excess of acid, but the second metal center does not protonate. The protonated complexes **8** and **9** can be deprotonated with equimolar diphenylguanidine base to give the unprotonated bimetallic compounds, **5** and **6**, as observed in a ^1H NMR spectrum of the solution. Even though the protonated compounds were insufficiently stable to give satisfactory elemental analyses or crystals, their spectra and deprotonations to the neutral bimetallic compounds strongly support the assignment of their structures.

The acid-catalyzed formation (Scheme I) of the bimetallic complexes from **1** or **2** must involve dissociation of the BT from the $\text{Cp}'(\text{CO})_2\text{Re}(\text{BT})$, and this dissociation must be promoted by the acid. Since both **1** and **2** exist as mixtures of the $\eta^1(\text{S})$ and 2,3- η^2 isomers, likely protonation sites are the metal in the 2,3- η^2 or $\eta^1(\text{S})$ isomer, or the sulfur atom of the 2,3- η^2 isomer. When **2**, a mixture of **2a** and **2b**, is reacted with a catalytic amount of $\text{CF}_3\text{SO}_3\text{H}$ in the presence of

excess PPh_3 , $\text{Cp}^*(\text{CO})_2\text{Re}(\text{PPh}_3)$ is formed almost immediately; no **2** remains and no bimetallic complex **5** is formed. The PPh_3 effectively traps the $\text{Cp}^*(\text{CO})_2\text{Re}$ fragment, and the BT is completely dissociated and uncoordinated. The PPh_3 does not react with **2** or **6** during this time frame when no acid is present. Since the interconversion between **2a** and **2b**⁴ is much slower than the acid-catalyzed reaction of **2** with PPh_3 , the acid must either catalyze this interconversion, or it must catalyze the substitution of BT by PPh_3 in both isomers.

Reaction of the methyl-substituted benzo[b]thiophene complex $\text{Cp}(\text{CO})_2\text{Re}(2\text{-MeBT})$ (**3**), which exists as only the S-bonded isomer, with $\text{CF}_3\text{SO}_3\text{H}$ gives the protonated monometallic complex **11**. Complex **3** protonates cleanly at the metal center; no bimetallic compound is formed and 2-MeBT is not dissociated. The compound was insufficiently stable over the time period required to record its ^{13}C NMR spectrum; so, it was not possible to determine if the protonated product had a *cis* or *trans* structure. Attempts to synthesize the bimetallic compound $[\text{Cp}(\text{CO})_2\text{Re}](\eta^2:\eta^1(\text{S})-\mu_2\text{-2-MeBT})[\text{Re}(\text{CO})_2\text{Cp}^*]$ from the reaction of **3** with $\text{Cp}^*(\text{CO})_2\text{Re}(\text{THF})$ were also unsuccessful. It appears that the 2-methyl group substantially reduces the coordinating ability of the 2,3-olefin, either by making the olefin a poorer π -acceptor or by sterically inhibiting metal-olefin bonding.

Protonation of $\text{Cp}(\text{CO})_2\text{Re}(\text{PPh}_3)$ (**4**) and ^1H -coupled, ^{13}C NMR Spectra of $[\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{ReH}]\text{O}_3\text{SCF}_3$ (**12**) and (**8**). Compound **4** was synthesized by literature methods¹⁰ analogous to the syntheses of **1** and **2**. When **4** is reacted at room temperature with $\text{CF}_3\text{SO}_3\text{H}$ in CD_2Cl_2

solution, an equilibrium mixture of *cis*-[Cp(CO)₂(PPh₃)Re(H)]O₃SCF₃ (**12a**) and *trans*-[Cp(CO)₂(PPh₃)Re(H)]O₃SCF₃ (**12b**) isomers is formed;¹³ in addition, some unprotonated **4** remains.¹³ Fluxionality of the complexes in solution is indicated by the lack of discernible ¹H or ¹³C NMR resonances for **4** and **12** at this temperature. Only broad, overlapping bands are present. However, upon cooling the solution to -60 °C, **4** and isomers of **12** are easily distinguished. Compound **12** exists in a 1:10 ratio of *cis:trans* isomers. The *cis* and *trans* isomers of **12** have been reported previously.¹³ In the ¹H NMR spectrum, the hydride resonance of the *cis* isomer **12a** (δ -7.83 (d, ¹J_{PH} = 41.7 Hz)) has a considerably larger J_{PH} coupling constant than the *trans* isomer **12b** (δ -8.86 (d, ¹J_{PH} = 14.7 Hz)). In the ¹H-coupled, ¹³C NMR spectrum, the one expected CO resonance of the *trans* isomer **12b** (δ 189.5 (d of d, ¹J_{PC} = 17.7 Hz, ¹J_{HC} = 13.2 Hz)) is easily detected, but the two CO resonances expected for the minor isomer **12a** (δ 196.0 and 190.6) are barely distinguishable due to the small amount of this isomer present.

Protonation of the bimetallic compound **5** gives the monoprotonated **8**, which exhibits the same type of fluxionality as **12** in solution in its ¹H and ¹³C NMR spectra at room temperature. Only broad overlapping bands are present. Upon cooling a solution of **8** to -60 °C, the ¹H and ¹³C NMR spectra indicate that only one isomer is present, and no unprotonated **4** remains. Since only one hydride resonance (δ -8.67) and two Cp resonances are observed in the ¹H NMR spectrum, and only four diastereotopic CO resonances (δ 201.8, 199.4, 189.9 and 188.9) and two Cp resonances (δ 89.3 and 88.5) are observed

in the $^{13}\text{C}\{^1\text{H}\}$ spectrum, only one isomer is distinguishable. In the ^1H -coupled, ^{13}C NMR spectrum of **8**, the two downfield carbonyl resonances remain sharp singlets, while the two upfield resonances become doublets (δ 190.0 (d, $^1J_{\text{HC}} = 13.4$ Hz) and 188.8 (δ , $^1J_{\text{HC}} = 13.9$ Hz)). The nearly equal $^1J_{\text{HC}}$ values for the carbonyls indicates a *trans* configuration of the CO's. In addition, the $^1J_{\text{HC}}$ values (13.4 Hz and 13.9 Hz) closely match the $^1J_{\text{HC}}$ value (13.2 Hz) for the *trans* carbonyls in **12** and further support the *trans* assignment for the carbonyl groups in **8**.

Structure of $[\text{Cp}(\text{CO})_2\text{Re}]_2(\eta^2:\eta^1(\text{S})-\mu_2\text{-BT})$ (**5**). In the structure of **5** (Figure 1) the coordinated BT sulfur has a trigonal-pyramidal geometry; it is roughly sp^3 hybridized. The sum of the angles around the sulfur (311 (1) $^\circ$) in **5** is smaller than that in the S-bonded BT complex $\text{Cp}^*(\text{CO})_2\text{Re}(\eta^1(\text{S})\text{-3-MeBT})$ (326 (1) $^\circ$).^{4b} The Re1-S distance of 2.35 (1) $\text{\AA}$ is similar to that (2.356 (4) $\text{\AA}$) of $\text{Cp}^*(\text{CO})_2\text{Re}(\eta^1(\text{S})\text{-3-MeBT})$.^{4b} The S-coordinated Re lies out of the plane of the BT such that the angle between the Re-S vector and the vector from S to the midpoint of the line between C3 and C8 is 118° . This angle is smaller than those in other S-coordinated thiophene complexes $\text{Cp}^*(\text{CO})_2\text{Re}(\eta^1(\text{S})\text{-3-MeBT})$ (131°)^{4b} and $\text{Cp}^*(\text{CO})_2\text{Re}(\eta^1(\text{S})\text{-T})$ (140°) (T = thiophene),²² but similar to those in $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\eta^1(\text{S})\text{-2-MeT})^+$ (119.1°)²³ and $\text{Cp}(\text{CO})_2\text{Fe}(\eta^1(\text{S})\text{-DBT})^+$ (119.4°) (DBT = dibenzothiophene).²⁴ Another structural aspect of **5** is the lengthening (~ 0.1 $\text{\AA}$) of S-C2 (1.81 (3) $\text{\AA}$) as compared to the corresponding S-C2 and S-C9 distances in 5-bromo-2,3-dimethylbenzo[b]thiophene (1.75 (1), 1.741 (9) $\text{\AA}$),²⁵ 3-formylbenzo[b]thiophene (1.704 (5), 1.733 (5)

Å),²⁶ CpRu(η^6 -BT)⁺ (1.72 (1), 1.730 (7) Å)²⁷ and CpRu(η^5 -BT•H) (1.723 (4), 1.764 (3) Å).²⁸ The other S-C bond (S-C9 = 1.77 (3) Å) appears to be only slightly lengthened by comparison. Lengthening of the analogous S-C2 bond in Cp*(CO)₂Re(η^1 (S)-3-MeBT) (S-C2 = 1.92 (2) Å) is also observed.^{4b} The lengthening of S-C bonds is particularly interesting since these bonds must be cleaved in BT HDS.

CONCLUSION

Previously, we showed that selenophene can coordinate to two metal complex fragments in **A**,⁵ and that benzo[b]thiophene can coordinate to Re and W in **B**.^{4b} In complexes **5**, **6**, and **7** (eqs 2 and 3),

A **B**

Cp'(CO)₂Re fragments are coordinated at both the sulfur and the 2,3-olefin bond. Spectroscopic data for these complexes strongly indicate that the BT sulfur is an electron donor atom, whereas the 2,3-olefin is a π electron acceptor. Thus, an electron-rich fragment such as Cp'(CO)₂Re coordinates favorably at the 2,3-olefin as a result of π -backbonding from the metal to the olefin. This backbonding also increases electron density on the sulfur, which makes it a better donor toward the Cp'(CO)₂Re fragment on the sulfur. Thus, metal binding at both sites moves electron density from the Cp'(CO)₂Re group coordinated to the olefin to the Cp'(CO)₂Re group coordinated to the sulfur. This makes the $\eta^1(\text{S})$ -coordinated Re sufficiently basic that it is readily protonated by CF₃SO₃H to give the series of complexes **8**, **9**, and **10**.

REFERENCES

- (1) Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences and Materials Science Divisions.
- (2) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61.
- (3) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387.
- (4) (a) Choi, M.-G.; Robertson, M. J.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 4005. (b) Choi, M.-G.; Angelici, R. J. *Organometallics* **1992**, *11*, 3328.
- (5) (a) Choi, M.-G.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7811. (b) Choi, M.-G.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 5651.
- (6) (a) *Experimental Organometallic Chemistry*; Wayda, A. L.; Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987. (b) Shriver, D. F.; Dreuzdon, M. A. *The Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.
- (7) Shirley, D. A.; Cameron, M. D. *J. Am. Chem. Soc.* **1952**, *74*, 664.
- (8) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804.
- (9) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.
- (10) Angelici, R. J.; Facchin, G.; Singh, M. M. *Syn. React. Inorg. Met.-Org. Chem.* **1990**, *20*, 275.

- (11) Einstein, F. W. B.; Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 53.
- (12) Zhuang J.-M.; Batchelor, R. J.; Einstein, F. W. B.; Jones, R. H.; Hader, R.; Sutton, D. *Organometallics* **1990**, *9*, 2723.
- (13) Panosyan, G. A.; Petrovskii, P. V.; Pyshnograyeva, N. I.; Kolobova, N. E.; Setkinga, V. N.; Fedin, E. I. *J. Organomet. Chem.* **1976**, *108*, 209.
- (14) a) Gilmore, C. J. *J. Appl. Cryst.* **1984**, *17*, 42. b) Deurskens, P. T. *Technical Report 1984/1 Crystallography Laboratory*, Toernooiveld, 65625 Ed Nijmegen, Netherlands.
- (15) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).
- (16) Ibers, J. A.; Hamilton, W. C. *Acta Crysta.* **1964**, *17*, 781.
- (17) Cromer, C. T. "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.3.1 (1974).
- (18) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corporation (1985).
- (19) Powell, D. R.; Jacobson, R. A. "FOUR: A Generalized Crystallographic Fourier Program", U. S. DOE Report IS-4737, Iowa State University, Ames, IA (1980).
- (20) (a) Takahashi, K.; Ito, I.; Matsuki, Y. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2316. (b) Hockett, S. C.; Angelici, R. J.; Ekman, M. E.; Schrader, G. L. *J. Catal.* **1988**, *113*, 36.

- (21) Clark, P. D.; Ewing, D. F.; Scrowston R. M. *Org. Magn. Reson.* **1976**, *8* 252.
- (22) Choi, M.-G.; Angelici, R. J. *Organometallics* **1991**, *10*, 2436.
- (23) Benson, J. W.; Angelici, R. J. *Organometallics* **1992**, *11*, 1992.
- (24) Goodrich, J. D.; Nickias, P. N.; Selegue, J. P. *Inorg. Chem.* **1987**, *26*, 3424.
- (25) Hogg, J. H. C.; Sutherland, H. H. *Acta Crystallogr. Sect. B* **1974**, *30*, 2058.
- (26) Pascard, P. R.; Pascard-Billy, C. *Acta Crystallogr. Sect. B* **1972**, *28*, 1926.
- (27) Hockett, S. C.; Miller, L. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1988**, *7*, 686.
- (28) Hockett, S. C.; Angelici, R. J. *Organometallics* **1988**, *7*, 1491.

**PAPER 2. SULFUR-COORDINATED THIOPHENE AND
BENZOTHIOPHENE IN $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{thiophene})^+$:
CONVERSION TO THIENYL AND THIENYLCARBENE
COMPLEXES¹**

ABSTRACT

A series of stable sulfur-coordinated thiophene complexes $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\eta^1(\text{S})\text{-Th})^+$, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{Th} = \text{thiophene (T), 2,5-Me}_2\text{T, benzo[b]thiophene (BT), and 2-MeBT}$, are prepared by the reaction of $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{ClCH}_2\text{Cl})^+$ with thiophenes. The T and BT complexes react with bases to abstract a proton from the 2-carbon of the $\eta^1(\text{S})$ -coordinated thiophenes to give neutral 2-thienyl (2-Tyl) or 2-benzothieryl (2-BTyl) complexes. Reaction of the 2,5-Me₂T complex with base results in proton abstraction at the 3-carbon to give the 3-(2,5-Me₂Tyl) complex. The 2-Tyl and 2-BTyl complexes react with $\text{CF}_3\text{SO}_3\text{H}$ to give cationic thienylcarbene and benzothierylcarbene

complexes, respectively, which are isomers of the starting $\eta^1(\text{S})$ -coordinated thiophene complexes. This series of facile reactions demonstrates that $\eta^1(\text{S})$ coordination can activate thiophenes in a way that leads to disruption of the aromaticity of the thiophene ligand upon formation of the thienylcarbene complexes. The base removal of a 2-proton from $\eta^1(\text{S})$ -thiophene ligands also suggests a mechanism for the exchange of these protons with deuterium during the hydrodesulfurization of thiophenes on heterogeneous catalysts.

INTRODUCTION

Of all the possible modes of thiophene adsorption^{2,3} at metal sites on heterogeneous catalysts during the hydrodesulfurization (HDS) of thiophene (T), the $\eta^1(\text{S})$ mode was one of the first to be proposed. Several transition metal complexes containing an $\eta^1(\text{S})$ -coordinated thiophene or benzo[b]thiophene (BT) have been reported,⁴ but there is

$\eta^1(\text{S})\text{-T}$

$\eta^1(\text{S})\text{-BT}$

no direct evidence that this mode of bonding activates the thiophene to undergo C-S bond cleavage, which is required in the HDS process.

(However, $(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{Rh}(\eta^1(\text{S})\text{-T})$ is a proposed intermediate in a reaction that leads to Rh insertion into a thiophene C-S bond.⁵)

There is also no direct evidence for cleavage of a C-H bond in $\eta^1(\text{S})$ -coordinated T or BT; such a cleavage would provide a model for the deuterium exchange of thiophene hydrogens, which is observed when thiophene is passed with D_2 over HDS catalysts.⁶

In the present study, we explore reactions of $\eta^1(\text{S})$ -coordinated thiophenes (Th) in $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\eta^1(\text{S})\text{-Th})^+$ complexes, which undergo C-H cleavage to give thienyl complexes. Upon reaction with acids, these thienyl complexes are converted to thienylcarbene

derivatives. These model reactions open new ways of thinking about the reactivity of thiophenes on HDS catalysts.

thienyl

thienylcarbene

EXPERIMENTAL SECTION

General Procedures. All reactions and manipulations were carried out under a N₂ atmosphere using standard Schlenk techniques⁷ unless stated otherwise. All solvents were reagent grade and dried under N₂ by the following standard methods.⁸ Diethyl ether (Et₂O) was distilled from Na/benzophenone. Hexanes and CH₂Cl₂ were distilled from CaH₂. Methanol was distilled from Mg/I₂. The neutral alumina (Brockman, activity I, ~150 mesh) used for chromatography was deoxygenated at room temperature under high vacuum overnight and then deactivated with 5% w/w deionized water and stored under N₂.

The ¹H and ¹³C NMR spectra were recorded on either a Nicolet NT-300 or a Varian VXR-300 spectrometer with CD₂Cl₂ as the internal lock and internal reference (δ 5.32 for ¹H and δ 53.8 for ¹³C). Fast atom bombardment (FAB) spectra were obtained on a Kratos MS-50 mass spectrometer. Infrared spectra were recorded in CH₂Cl₂ on a Nicolet 710 FT-IR spectrophotometer. Elemental analyses were performed by either Desert Analytics or Galbraith Laboratories, Inc.

Thiophene (T) was purified by a published method.⁹ Triflic acid, CF₃SO₃H, was distilled over P₂O₅ under dry argon. Cp(NO)(PPh₃)Re(CH₃)¹⁰ and 2-methylbenzo[b]thiophene (2-MeBT)¹¹ were prepared by literature methods. All other reagents were used as received from commercial sources. ¹H and ¹³C NMR data of the compounds is tabulated at the end of the Experimental section in Tables I and II.

[Cp(NO)(PPh₃)Re(η^1 (S)-T)]BF₄ (**1**). Compounds **1-4** containing an η^1 (S)- bonded thiophene were prepared by a method similar to that previously reported by Gladysz and co-workers.¹² A solution of Cp(NO)(PPh₃)Re(CH₃) (0.210 g, 0.375 mmol) in 20 mL of CH₂Cl₂ was cooled to -78 °C. Then HBF₄•OEt₂ (80 mL, 0.40 mmol) was added to the solution with stirring; the color of the solution turned from bright orange to dark orange-brown. After stirring for 2 minutes, thiophene (60 mL, 0.75 mmol) was added to the solution, which was stirred and slowly warmed to room temperature over an 8 hour period. Solvent was then removed under vacuum to leave an oily brown residue. The residue was taken up in ~20 mL CH₂Cl₂ and filtered through a short plug of Celite. The brown solution was cooled to 0 °C, and 20 mL of Et₂O was added to precipitate [Cp(NO)(PPh₃)Re(η^1 (S)-T)]BF₄ (0.162 g, 61%) as a moderately air-stable tan solid, ν (NO) 1724 cm⁻¹. Anal. Calcd. for C₂₇H₂₄BF₄NOPReS: C, 45.20; H, 3.38. Found: C, 44.62; H, 3.34.

[Cp(NO)(PPh₃)Re(η^1 (S)-2,5-Me₂T)]BF₄ (**2**). This complex was prepared analogously to **1** from Cp(NO)(PPh₃)Re(CH₃) (0.150 g, 0.269 mmol) and 2,5-Me₂T (61 mL, 0.54 mmol) to give **2** as a brown powder (0.068 g, 39%). ν (NO) 1720 cm⁻¹.

[Cp(NO)(PPh₃)Re(η^1 (S)-BT)]BF₄ (**3**). Compound **3** was prepared in the same manner as for **1** using Cp(NO)(PPh₃)Re(CH₃) (0.200 g, 0.358 mmol) and BT (0.098 g, 0.72 mmol) to give **3** as a moderately air-stable pale mustard yellow powder (0.21 g, 78%). ν (NO) 1721 cm⁻¹. FAB m/e 677 (M⁺), based on ¹⁸⁷Re.

[Cp(NO)(PPh₃)Re(η^1 (S)-2-MeBT)]BF₄ (4). This complex was prepared in the same manner as **1** using Cp(NO)(PPh₃)Re(CH₃) (0.175 g, 0.313 mmol) and 2-MeBT (0.11 g, 0.74 mmol). Excess 2-MeBT was sublimed from the residue under vacuum before the filtration step. Compound **4** was isolated as a moderately air-stable brown-orange powder (0.14 g, 57%). $\nu(\text{NO})$ 1721 cm⁻¹.

Cp(NO)(PPh₃)Re(2-Tyl) (5). Compound **1** (0.108 g, 0.151 mmol) was suspended in 5 mL of methanol. Crushed KOH pellets (0.021 g, 0.38 mmol) were added with stirring. The suspension turned from brown to orange within 60 seconds. The methanol was removed under vacuum, and the orange residue was dissolved in a 2:1 mixture of hexanes:CH₂Cl₂. This solution was chromatographed on neutral alumina, and an orange band was eluted using a 2:1 hexanes:CH₂Cl₂ solution. The volume of the orange solution was reduced to ~10 mL under vacuum, precipitating an orange solid. The clear colorless solvent was decanted, and the air-stable orange powder **5** was dried under vacuum (0.057 g, 60%). $\nu(\text{NO})$ 1653 cm⁻¹. Anal. Calcd. for C₂₇H₂₃NOPReS: C, 51.52; H, 3.69. Found: C, 51.83; H, 3.43.

Cp(NO)(PPh₃)Re[3-(2,5-Me₂Tyl)] (6). This compound was prepared in the same manner as **5**, using **2** (0.040 g, 0.054 mmol) and KOH (0.006 g, 0.1 mmol) in methanol to give **6** as an orange solid (0.011 g, 28%). $\nu(\text{NO})$ 1655 cm⁻¹.

Cp(NO)(PPh₃)Re(2-BTyl) (7). In the same manner as **5**, using **3** (0.100 g, 0.144 mmol) and KOH (0.021 g, 0.38 mmol) in methanol, **7** was prepared as an orange powder (0.035 g, 36%). $\nu(\text{NO})$ 1653 cm⁻¹.

Anal. Calcd. for $C_{31}H_{25}NOPReS$: C, 54.80; H, 3.72. Found: C, 54.14; H, 3.42.

$Cp(NO)(PPh_3)Re[3-(2-MeBTyl)]$ (**8**). Compound **8** was prepared in the same manner as **5**, using **4** (0.050 g, 0.072 mmol) and KOH (0.011 g, 0.20 mmol) in methanol. Compound **8** was isolated as an orange powder (0.010 g, 20%), $\nu(NO)$ 1653 cm^{-1} . However, **8** is not stable as indicated by the gradual color change of the CD_2Cl_2 solution from clear orange to a cloudy dark brown during a period of a few minutes. In an 1H NMR spectrum of the solution, free 2-MeBT appeared, based on the presence of the methyl resonance at 2.58 ppm.

$[Cp(NO)(PPh_3)Re(2-Tylcarbene)]O_3SCF_3$ (**9**). A 5 mm NMR tube was charged with **5** (0.018 g, 0.029 mmol) and 0.55 mL of CD_2Cl_2 . Then, CF_3SO_3H (2.6 mL, 0.029 mmol) was added, and the tube was shaken. The solution immediately changed from clear orange to clear yellow. An 1H NMR spectrum of the solution showed nearly quantitative conversion to **9**. $\nu(NO)$ 1716 cm^{-1} . Compound **9** was characterized spectroscopically as discussed in the Results and Discussion. Compound **9** is not stable as indicated by the change in solution color from clear yellow to green-yellow after several minutes. Attempts to isolate the compound out of solution were unsuccessful.

$[Cp(NO)(PPh_3)Re(2-BTylcarbene)]O_3SCF_3$ (**10**). Compound **10** was prepared in the same manner as **9** using **7** (0.015 g, 0.022 mmol) and CF_3SO_3H (2 mL, 0.022 mmol). The color of the solution immediately changed from clear orange to clear ruby red upon addition of the CF_3SO_3H . A 1H NMR spectrum of the solution showed nearly

quantitative conversion to **10**. $\nu(\text{NO})$ 1720 cm^{-1} . Compound **10** behaved similarly to compound **9** and could not be isolated from solution. It was characterized spectroscopically, as discussed in detail later.

Table I. ^1H NMR Data (δ) for Complexes in $\text{CD}_2\text{Cl}_2^{\text{a}}$

	PPh_3^{b}		Th or BT ^b		Cp	Me
1	7.56 (m),	7.27 (m)	7.22 (m),	6.91 (m,2H)	5.42 (s,5H)	
2	7.49 (m),	7.28 (m)	6.69 (s,2H)		5.29 (s 5H)	1.95 (s,6H)
3	7.60 (m)		7.80 (m,2H),	7.36 (m,3H),	5.23 (s,5H)	
			6.27 (d,1H) ^c			
4	7.54 (m),	7.26 (m)	7.69 (d,1H) ^d ,	7.42 (d,1H) ^e	5.32 (s,5H)	2.37 (d,3H) ^g
			7.10 (s, 1) ^d ,	6.73 (d,1H) ^{d,f}		
5	7.36 (s)		7.07 (d,1H) ^h ,	6.69	5.18 (s,5H)	
			(d of d,1H) ⁱ ,	6.36 (d,1H) ^j		
6	7.35 (s)		5.51 (s,1H)		5.12 (s,5H)	2.40 (s,3H),
						2.08 (s,3H)
7	7.36 (s)		7.21 (d,1H) ^d ,	7.22 (d,1H) ^d ,	5.26 (s,5H)	
			7.04 (t of d,1H) ^k ,			
			6.84 (t of d,1H) ^d ,	6.44 (s,1H)		
8	7.44 (m)		7.65 (m,2H),	7.55 (d,1H) ^d	5.25 (s,5H)	3.95 (d,3H) ^g

Table 1 (continued)

9	7.55 (m), 7.24 (m)	7.37 (d,1H) ^l , 6.80 (d,1H) ^l ,	5.78 (s,5H)
		4.97 (d,1H) ^m , 4.11 (d,1H) ^m	
10	7.57 (m), 7.36 (m)	7.20 (m,1H), 4.84 (d,1H) ⁿ ,	5.90 (s,5H)
		3.81 (d,1H) ^{n,f}	

^aAll coupling constants are J_{HH} values. ^bSome overlap of PPh₃, thiophene, and benzothiophene resonances occurs. ^cJ=5.7 Hz. ^dJ=7.8 Hz. ^eJ=7.5 Hz. ^fOne or more proton signals are apparently contained in the PPh₃ multiplet. ^g1.2 Hz. ^hJ=4.8 Hz. ⁱJ=4.8 Hz and 3.0 Hz. ^jJ=3.0 Hz. ^kJ=7.8 and 1.2 Hz. ^lJ=5.4 Hz. ^mOn C3, J=24 Hz. ⁿOn C3, J=26 Hz.

Table II. ^{13}C NMR Data for Complexes in CD_2Cl_2 .

	PPh ₃ ^a	Th or BT	Cp	Me
1	133.9 (d), 133.6 (d), 132.5 (d), 129.9 (d)	138.3, 132.4	93.3	
2	133.8 (d), 133.6 (d), 132.2 (d), 129.8 (d)	130.1, 129.5	93.2	14.9
3	133.6 (d), 132.6 (d), 132.4 (d), 129.9 (d)	148.3 (d) ^b , 138.7, 131.8, 130.9, 129.5, 128.3, 126.8, 124.3	93.7	
4	133.2 (d), 132.6 (d), 131.8 (d), 129.4 (d)	148.1, 144.6, 139.8, 128.9, 127.3, 126.5, 125.3, 123.6	93.6	15.3
5	135.8 (d), 134.1 (d), 130.4 (d), 128.4 (d)	136.0 (d) ^c , 128.4, 127.5 (d) ^d , 127.3	91.4	
6	136.6 (d), 134.0 (d), 130.5 (d), 128.5 (d)	142.3, 133.2, 132.6, 126.0 (d) ^e	91.8	19.0, 14.8
7	136.3 (d), 134.1 (d), 130.2 (d), 128.3 (d)	146.7, 146.4, 136.6 (d) ^f , 131.7 (d) ^c , 122.5, 119.7 (d) ^g , 119.1	90.6	
9	133.2 (d), 132.4, 130.2 (d), 129.5 (d)	268.7 ^h , 150.5, 146.2, 56.6 ⁱ	97.3	

Table II (continued)

10	133.1 (m), 132.6 (d), 129.8 (d)	278.5 (d) ^{h,i} , 144.5, 142.0, 128.4, 127.1, 124.0, 120.5, 67.3 ⁱ	98.5
----	------------------------------------	---	------

^aTypical coupling constants for PPh₃ in 1-10: J_{PCa}=56.9 Hz; J_{PCb}=10.7; J_{PCg}=2.7 Hz; J_{PCd}=11.3 Hz. ^bJ_{PC}=2.7 Hz. ^cJ_{PC}=2.2 Hz. ^dJ_{PC}=9.7 Hz. ^eJ_{PC}=8.4 Hz. ^fJ_{PC}=10.2 Hz. ^gJ_{PC}=6.5 Hz. ^hC2. ⁱC3. ^jJ_{PC}=7.8 Hz.

RESULTS AND DISCUSSION

Synthesis of $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\eta^1(\text{S})\text{-Th})^+$ Complexes (1-4). The thiophene-containing complexes $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\eta^1(\text{S})\text{-Th})^+$ (1-4) were synthesized in a manner similar to that used for the $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{L})^+$ complexes,¹² where L can be one of many two-electron donor ligands, including dialkyl sulfides CH_3SR , where R = CH_3 , Et, *i*-Pr, and Bu^t.¹³ Thus, $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{CH}_3)$ and $\text{HBF}_4 \cdot \text{OEt}_2$ are reacted in CH_2Cl_2 at -78°C to generate the reactive complex $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{ClCH}_2\text{Cl})^+$. In this complex, the very weakly coordinated CH_2Cl_2 ligand¹² is displaced by a thiophene to give the $\eta^1(\text{S})$ -bonded thiophene complex (eq 1).

Compounds 1-4 were characterized by FT-IR, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR, FAB mass spectrometry, and elemental analyses (see Experimental Section and Tables I and II). The $\nu(\text{NO})$ absorption in the FT-IR spectra of these cationic compounds is $\sim 90\text{ cm}^{-1}$ higher than the band in the neutral starting material, $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{CH}_3)$ ($\nu(\text{NO}) = 1630\text{ cm}^{-1}$). The Cp resonances in the ^1H NMR spectra are downfield ($\sim 0.3\text{ ppm}$) as compared to that of $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{CH}_3)$ ($\delta\ 4.95$). The thiophene ring protons in 1 are upfield ($\sim 0.2\text{ ppm}$) of those in free T ($\delta\ 7.37\text{ (m)}$ and 7.14 (m)). These resonances are also slightly upfield of those in the

two similar complexes $\text{Cp}^*(\text{CO})_2\text{Re}(\eta^1(\text{S})\text{-T})^{14}$ and $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\eta^1(\text{S})\text{-T})^+.$ ¹⁵ If the thiophene ligands in complexes **1-4** were bound to the metal in an η^2 fashion through one of the C-C double bonds, the thiophene ring proton signals would be expected to shift significantly upfield, as reported for complexes of η^2 -thiophene,¹⁶ η^2 -selenophenes,¹⁷ η^2 -benzo[b]thiophene,¹⁸ and olefins.¹⁹ In the ^{13}C NMR spectra of complexes **1-4**, the thiophene carbon resonances are slightly downfield of those in free thiophene, as was also observed for $\text{Cp}(\text{CO})_2\text{Fe}(\eta^1(\text{S})\text{-T})^+,$ ²⁰ $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\eta^1(\text{S})\text{-T})^+,$ ¹⁵ $\text{Cp}(\text{CO})_2\text{Ru}(\eta^1(\text{S})\text{-T})^+,$ ⁴ and $\text{Cp}(\text{CO})_2\text{Re}(\eta^1(\text{S})\text{-T}).$ ¹⁴ Again, an upfield shift in the ^{13}C resonances would have been expected¹⁶⁻¹⁹ for the η^2 -bonded carbons if the thiophenes were η^2 -bonded. Thus, the NMR spectra establish that the thiophenes, including the benzo[b]thiophenes, in compounds **1-4** are $\eta^1(\text{S})$ -bonded. This type of coordination is confirmed by X-ray diffraction studies of $\text{Cp}^*(\text{CO})_2\text{Re}(\eta^1(\text{S})\text{-T})^{14}$, $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(\eta^1(\text{S})\text{-2-MeT})^+,$ ¹⁵ and $\text{Cp}^*(\text{CO})_2\text{Re}(\eta^1(\text{S})\text{-3-MeBT}).$ ^{18b}

Synthesis of $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{Thienyl})$ Complexes (**5-8**). A proton can be abstracted from the $\eta^1(\text{S})$ -bonded thiophene ligands in complexes **1-4** with KOH in methanol to give the corresponding thienyl complexes **5-8** (eq 2). Conversion from the cationic complex to the

neutral thienyl compound is immediate, as evidenced by a change in color of the suspension from brown to orange. The $\nu(\text{NO})$ band in the FT-IR spectrum of **5** at 1653 cm^{-1} is 70 cm^{-1} lower than that of the starting $\eta^1(\text{S})$ thiophene complex **1** ($\nu(\text{NO}) = 1724\text{ cm}^{-1}$). The $\nu(\text{NO})$ bands of the other thienyl compounds **6-8** also shift $\sim 70\text{ cm}^{-1}$ to lower wavenumbers as compared to their starting cationic complex. In the ^1H NMR spectrum of **5**, only 3 thiophenic proton resonances are observed: two doublets and a doublet of doublets. This pattern is consistent with the assignment of **5** as a 2-thienyl (2-Tyl) complex and is similar to those in $\text{Cp}_2\text{Zr}(\text{2-Tyl})_2$, $\text{Cp}_2\text{Ti}(\text{2-Tyl})_2$,²¹ and $\text{Cp}^*(\text{PMe}_3)(\text{Cl})\text{Rh}(\text{2-Tyl})$,⁵ whose structure has been established unequivocally by an X-ray diffraction investigation. In addition, the Cp resonance of **5** shifts upfield from 5.42 ppm in **1** to 5.18 ppm in **5**, again indicative of the change from a cationic compound to a neutral species. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5**, all four thienyl carbons are observed. However, unlike in the $\eta^1(\text{S})$ -bonded compound **1** where the four thiophene carbons are all singlets, two of the carbons in **5**, presumably C2 and C3, are split into doublets by the phosphorus in the PPh_3 ligand (see Table II). These one- and two-bond couplings ($J_{\text{PC}} = 9.7$ and 2.2 Hz , respectively) to the phosphorus again support the structure in which the C2 carbon is bonded to the metal to give the 2-thienyl complex.

The FT-IR, ^1H NMR, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{2-BTyl})$ (**7**) establish a structure with a 2-benzo[b]thienyl (2-BTyl)

ligand. In the ^1H NMR spectrum of **7**, the pattern of singlets, doublets, and triplets of the BTyl protons (Table I) is well resolved and is similar to the resonances in the BTyl complexes $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Ru}(2\text{-BTyl})$ and $\text{Cp}(\text{PMe}_3)_2\text{Ru}(2\text{-BTyl})$.²² In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7**, the C2, C3 and C7 signals are split into doublets by the phosphorus in the PPh_3 ligand, again similar to the previously cited 2-BTyl complexes. All of these spectral data are consistent with bonding of the C2 carbon of the BTyl ligand to the metal.

In compounds **2** and **4** containing $\eta^1(\text{S})$ -2,5- Me_2T and $\eta^1(\text{S})$ -2-MeBT ligands, respectively, no H2 proton is present, which eliminates the possibility of forming 2-Tyl and 2-BTyl complexes upon deprotonation by base. When compounds **2** and **4** are reacted with KOH in methanol, the H3 proton is abstracted to give $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}[3\text{-(2,5-Me}_2\text{Tyl)}]$ (**6**) and $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}[3\text{-(2-MeBTyl)}]$ (**8**), respectively. In compound **2**, the two methyl groups of the 2,5- Me_2T ligand are

diastereotopic and therefore could give separate NMR signals, but only one singlet is observed at ambient temperature in the ^1H NMR (δ 1.95 (s)) and ^{13}C NMR (δ 14.9) spectra, presumably as a result of rapid inversion at the sulfur atom.^{4,15,20,23} When **2** is converted to the 3-(2,5- Me_2Tyl) complex **6**, the methyl groups are now inequivalent and

are observed as two distinct singlets in the ^1H NMR (δ 2.40 (s) and 2.08 (s)) and ^{13}C NMR (δ 19.0 and 14.8) spectra of the compound. In the ^1H NMR spectra, the single H4 proton is shifted significantly upfield from δ 6.69 (s) in **2** to δ 5.51 (s) in **6**. The analogous 3-(2-MeBTyl) compound **8** is not sufficiently stable in solution to obtain a satisfactory ^{13}C NMR spectrum. Presumably, the bulkiness of the 2-MeBTyl and PPh_3 ligands makes the compound unstable. However, an ^1H NMR spectrum shows peaks ascribable to 3-(2-MeBTyl) [Table I] as well as only one Cp (δ 5.25 (s)) and one methyl group (δ 3.95 (s)).

Two mechanisms may be considered for the base-promoted transformation (eq 2) from the $\eta^1(\text{S})$ complex to the thienyl complex (Scheme I). One (path a, Scheme I) involves initial deprotonation of the most acidic hydrogen at the C2 carbon to give a carbanionic center which rapidly migrates to the Re to give the 2-thienyl product. Coordination of the thiophene to the electron-withdrawing metal may make the proton on C2 more acidic than it is in free thiophene or benzo[b]thiophene. Thus, the conversions of **1-4** to **5-8** are complete within 60 seconds while free T^{24} and BT^{25} undergo much slower base-catalyzed deuterium exchange at ambient temperature. In the cases where there is no C2 proton, as in the 2,5-Me₂T(**2**) and 2-MeBT(**4**)

Scheme I

complexes, path *a* would require Re migration from the sulfur to the deprotonated C3 carbanion. While not impossible, a migration from the 1-position to the 3-position seems unlikely.

The other mechanism (path *b*, Scheme I) involves initial migration of the Re atom from the sulfur to the 2,3-olefin bond of the thiophene. Since there is no spectroscopic evidence for 2,3- η^2 coordination in complexes **1-4**, they would have to be present at low concentrations. However, such a migration is supported by the existence of 2,3- η^2 -olefin-coordinated thiophene in $\text{Os}(\text{NH}_3)_5(2,3\text{-}\eta^2\text{-T})^{2+}$.¹⁶ Also, the BT ligand in $\text{Cp}(\text{CO})_2\text{Re}(\text{BT})$ ¹⁸ exists as an equilibrium mixture of the $\eta^1(\text{S})$ and 2,3- η^2 isomers. In addition, the selenium analog of thiophene forms a complex $\text{Cp}^*(\text{CO})_2\text{Re}(\text{Sel})$ ¹⁷ in which the selenophene (Sel) is 2,3- η^2 -bonded to the Re. In other $\text{Cp}'(\text{CO})_2\text{Re}(\text{selenophene})$ complexes,¹⁷ the $\eta^1(\text{Se})$ and 2,3- η^2 isomers both are present in solution, the relative amounts depending on the number of methyl groups in the Cp' ligand and the degree of methyl

substitution on the selenophene. And isomerization between $\eta^1(\text{Se})$ and 2,3- η^2 isomers is possible even though only one isomer is observed spectroscopically. This was established for $\text{Cp}^*(\text{CO})_2\text{Re}(2,3\text{-}\eta^2\text{-SeI})$,¹⁷ in which the Re rapidly migrates from the 2,3-olefin to the 4,5-olefin bond, presumably through an $\eta^1(\text{Se})$ -coordinated intermediate. Although there is no evidence for this fluxionality in complexes **1-4**, the protons on the 2,3-carbons of the postulated 2,3- η^2 isomer should be easily removed to give the product thienyl complexes, as has been demonstrated in the deprotonation of alkene²⁶ and cycloalkene²⁷ complexes of $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}^+$ with KO^tBu to give the corresponding vinyl complexes (eq 3). Deprotonation of either the

2- or 3-proton of the postulated 2,3- η^2 isomers of the $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{Th})^+$ complexes provides a reasonable route to both the 2- and 3-thienyl complexes found in the reactions of **1-4** with KOH in methanol. Thus, path *b* (Scheme I) appears to be the most likely mechanism for the reaction in eq 2.

Bases besides KOH in methanol are also effective in deprotonating the $\eta^1(\text{S})$ -coordinated thiophene in **1**. Triethylamine ($\text{pK}_a = 11.01$ in H_2O)²⁸ effects the transformation (eq 2) almost immediately when an excess of the base is reacted with **1** in CD_2Cl_2 at room temperature in an NMR tube experiment; in contrast, pyridine ($\text{pK}_a = 5.25$ in H_2O)²⁸

does not give **5** under these conditions, even after several hours. Sources of H^- , such as $LiHBEt_3$ and $HFe(CO)_4^-$, do convert **1** to **5** immediately in CH_2Cl_2 solution. In all of these conversions of **1** to **5** a competing reaction is displacement of the $\eta^1(S)$ -bonded thiophene by the base. For example, the reaction of **1** with $LiHBEt_3$ produces both the thienyl complex **5** and the hydride complex $Cp(NO)(PPh_3)Re(H)^{29}$ in about equal proportions. A solution of compound **1** when stirred with neutral alumina or passed down a column of neutral alumina is also converted to the thienyl complex **5**. However, there is also decomposition of the starting compound **1** on the alumina. The best reagent for promoting the conversions of the $\eta^1(S)$ -thiophene complexes to their thienyl analogs (eq 2) is KOH in methanol.

In an effort to explore Diels-Alder reactivity of $\eta^1(S)$ -coordinated thiophene, **1** was reacted in solution with dienophiles, such as maleic anhydride and 4-phenyl-1,2,4-triazoline-3,5-dione, up to temperatures of 190 °C and pressures of 800 psi. However, no Diels-Alder products were observed; compound **1** either did not react, or the thiophene was simply displaced.

Reactions of $Cp(NO)(PPh_3)Re(2-Tyl)$ and $Cp(NO)(PPh_3)Re(2-BTyl)$ with CF_3SO_3H . The thienyl compound **5** reacts with one equivalent of triflic acid, CF_3SO_3H , in CD_2Cl_2 in a 5 mm NMR tube to give the cationic thienylcarbene complex **9** (eq 4) in nearly quantitative yield as determined by a 1H NMR spectrum. The reaction is instantaneous, as observed by the immediate color change of the clear solution from orange to bright yellow. While **9** is not sufficiently stable to be

isolated, it was characterized spectroscopically. The $\nu(\text{NO})$ band in the FT-IR spectrum of **9** (1716 cm^{-1}) is 63 cm^{-1} higher than that in the neutral thienyl compound **5**. In the ^1H NMR spectrum of **9**, two of the thienylcarbene protons are shifted significantly upfield (δ 4.97 (d, $J_{\text{HH}} = 24\text{ Hz}$) and 4.11 (d, $J_{\text{HH}} = 24\text{ Hz}$)) and are assigned as the two diastereotopic hydrogens on the C3 atom on the basis of their large mutual coupling constant. Also, the Cp resonance shifts downfield from 5.18 ppm in **5** to 5.78 ppm in **9**. In addition, no metal hydride resonance is observed at high field (up to -30 ppm), even at $-60\text{ }^\circ\text{C}$. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9**, the C2 alkylidene resonance is observed at 268.7 ppm, which is similar to the alkylidene resonance (δ 275.5) of the related compound $\text{Cp(NO)(PPh}_3\text{)Re(=CHSCH}_3\text{)}^+$.³⁰ The resonance of the C3 carbon, which is now sp^3 hybridized, is shifted upfield (δ 56.6) while the C4 and C5 olefin carbons (δ 150.5 (s) and 146.2 (s)) shift slightly downfield compared to those in the thienyl compound **5** (see Table II).

The BTyl compound $\text{Cp(NO)(PPh}_3\text{)Re(BTyl)}$ (**7**) also protonates at the C3 carbon when reacted with one equivalent of $\text{CF}_3\text{SO}_3\text{H}$ to give the benzothienylcarbene complex $\text{Cp(NO)(PPh}_3\text{)Re(BTylcarbene)}^+$ (**10**). In this case, the solution of **7** turns from orange to ruby red immediately

upon addition of the acid. The infrared spectrum of **10** shows a shift of the $\nu(\text{NO})$ band to higher wavenumbers (1653 cm^{-1} to 1720 cm^{-1}). The ^1H NMR spectrum of **10** again has resonances for the two diastereotopic hydrogens (δ 4.84 (d, 26 Hz) and 3.81 (d, 26 Hz)) on the C3 carbon. The Cp resonance of **10** (δ 5.90) is downfield of the resonance in the neutral BTyl complex **7** (δ 5.26). In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **10**, the resonance for the alkylidene carbon C2 is characteristically shifted downfield (δ 278.5 (d, $^2J_{\text{PC}} = 26\text{ Hz}$)) and, in this case, is split ($J_{\text{PC}} = 7.8\text{ Hz}$) by the phosphorus of the PPh_3 ligand. The resonance for the sp^3 hybridized C3 carbon is shifted upfield (δ 67.3), similar to shifts in the thienylcarbene complex **9**.

Both carbene complexes **9** and **10** were deprotonated with one equivalent of KOBU^t in CD_2Cl_2 in an NMR tube experiment within several minutes to give back the 2-thienyl complexes **5** and **7**, respectively, as the major products (>70%) (eq 5). This same type of acid/base chemistry has been observed previously by Gladysz and co-workers with the alkylidene complexes $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}[\text{=CH}(\text{CH}_2\text{R})]^+$, where $\text{R} = \text{H}$, CH_3 , or $n\text{-C}_3\text{H}_7$.³¹ These complexes were deprotonated with KOBU^t at the b-carbon to give the corresponding vinyl complexes $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(-\text{CH=CHR})$.

Complexes **9** and **10** were not sufficiently stable to be isolated for elemental analysis. Attempts to work-up solutions of the complexes resulted in darkening of the color of the compounds with decomposition. Attempts to grow crystals by slow vapor diffusion of hexanes or diethyl ether into a CH_2Cl_2 solution of the compound

resulted only in an intense green solution and residue that contained many products, none of which were the carbene or thienyl compounds. Unstable alkylidene complexes can often be stabilized by addition of a suitable nucleophile to the carbene carbon.³² In an attempt to isolate a stable adduct of **9**, a CD₂Cl₂ solution of **9** was reacted with equimolar PPh₂Me in a 5 mm NMR tube. A ³¹P NMR spectrum of the solution taken immediately after reaction showed that **9** and the PPh₂Me were consumed, and a mixture of products had formed. Even though the alkylidene complexes **9** and **10** could not be isolated from solution, their spectral data support the assignment of **9** as the thienylcarbene complex and **10** as the benzothienylcarbene analog.

It is somewhat surprising that the thienylcarbene complexes even form (eq 4), because it involves disruption of the aromaticity of the thiophene ring. In the related phenyl complex Cp(NO)(PPh₃)Re(C₆H₅),^{33,34} reaction with acid yields the η²-benzene complex (eq 5). Similarly, when the ruthenium BTyl complexes

CpL₂Ru(BTyl)²² are reacted (eq 6) with CF₃SO₃H, the Ru-C bond is cleaved, and the proton adds to the 2-position of the BTyl ligand to give the η¹(S)-coordinated benzothiophene complexes. Thus, in the reactions of

$\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{C}_6\text{H}_5)$ and $\text{CpL}_2\text{Ru}(\text{BTyl})^+$ complexes, the aromaticity of the phenyl group and BTyl group, respectively, are maintained by cleaving the metal carbon bond while forming the benzene and benzothiophene ligands. In contrast, protonation of complexes **5** and **7** do not result in cleavage of the Re-C bond but formation of the thienylcarbene complexes instead. It is not clear why these complexes behave differently. It is interesting that the $\eta^1(\text{S})$ thiophene complexes **1** and **3** are isomers of the thienyl complexes **9** and **10**. The isomerization of one form to the other has not been observed; so, it is not known which isomer is the most stable.

CONCLUSION

Comments on the Mechanism of D₂ Exchange of Thiophene over HDS

Catalysts. Catalytic reactor and organometallic model compound studies^{6,35} have shown that deuterium exchange (eq 7) with thiophene

over HDS catalysts occurs most readily in the 2 and 5 positions with lesser amounts of exchange at the 3 and 4 positions. Thiophenes also undergo exchange with deuterio-acids, including those generated by reaction of D₂ with (CpMo)₂(S₂CH₂)(μ-S)(S-H)⁺.³⁶ Rates of deuterium exchange in the η⁵-bound thiophene in the model complex CpRu(η⁵-T)⁺³⁶ follow the same trends. Therefore, the η⁵-coordination mode offers a reasonable explanation for the exchange on HDS catalysts. The base-promoted conversion of η¹(S) thiophene to a thienyl ligand reported in this paper provides the basis for another explanation for the rates of deuterium exchange of thiophenes over HDS catalysts (Scheme II). This exchange could proceed by η¹(S) adsorption of the thiophene on the catalyst surface. Then, deprotonation at either the 2,5 or 3,4 positions of the thiophene by a basic oxide, sulfide, or hydride ion would give a surface thienyl species; this step is similar to the reaction in eq 2 and Scheme I. Transfer of D⁺ from an acidic surface site, e. g. S-D^{d+}, formed in the reaction of D₂ with surface sulfur atoms, to the S-bonded carbon of

the 2- or 3-thienyl group would give the 2- or 3-deuterated thiophene; this step is modeled by the reaction in eq 6. While Cowley previously proposed a mechanism^{22,37} very similar to this, the reactions in eqs 2 and 6 provide examples of these reactions which actually occur at metal centers.

Scheme II

We sought to observe deuterium exchange into the thiophene ligand of $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\eta^1(\text{S})\text{-T})^+$ when it was dissolved in MeOD with one equivalent of pyridine base catalyst. Unfortunately, no exchange was observed when the solution was allowed to sit for 24 hours. Stronger bases such as NEt_3 under the same conditions simply converted **1** to **5** (eq 2). Thus, while both steps *a* and *b* in Scheme II have not been observed in a single metal complex, the separate reactions (eqs 2 and 5) suggest that the thienyl species are logical intermediates in the deuterium exchange of thiophene⁶ and benzo[b]thiophene³⁸ on HDS catalysts.

REFERENCES

- (1) Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division.
- (2) a) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387. b) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61.
- (3) Rauchfuss, T. B. *Prog. Inorg. Chem* **1992**, *39*, 259.
- (4) Benson, J. W.; Angelici, R. J. *Organometallics* **1993**, *12*, 680, and references therein.
- (5) Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151.
- (6) a) Kieran, P.; Kemball, C. *J. Catal.* **1965**, *4*, 1306. b) Blake, M. R.; Eyre, M.; Moyes, R. B. ; Wells, P. B. *Stud. Surf. Sci. Catal.* **1981**, *7*, 591. c) Smith, G. V.; Hinckley, C. C.; Behbahany, F. *J. Catal.* **1973**, *30*, 218. d) McCarty, K. F.; Schrader, G. L. *J. Catal.* **1987**, *103*, 261. e) Benson, J. W.; Schrader, G. L.; Angelici, R.J. *J. Catal.*, submitted for publication.
- (7) (a) *Experimental Organometallic Chemistry*, Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society, Washington, DC, 1987. (b) Shriver, D. F.; Drezzdon, M. A. *The Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.
- (8) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1980.

- (9) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897.
- (10) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.
- (11) Shirley, D. A.; Cameron, M. D. *J. Am. Chem. Soc.* **1952**, *74*, 664.
- (12) Fernandez, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207.
- (13) Quirós Méndez, N.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1991**, *10*, 2199.
- (14) (a) Choi, M.-G.; Angelici, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 8753.
(b) Choi, M.-G.; Angelici, R. J. *Organometallics* **1991**, *10*, 2436.
- (15) Benson, J. W.; Angelici, R. J. *Organometallics* **1992**, *11*, 922.
- (16) Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 5969.
- (17) (a) Choi, M.-G.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7811.
(b) Choi, M.-G.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 5651.
- (18) (a) Choi, M.-G.; Robertson, M. J.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 4005. (b) Choi, M.-G.; Angelici, R. J. *Organometallics* **1991**, *11*, 3328.
- (19) (a) Burns, C. J.; Anderson, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 915.
(b) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.
- (20) Goodrich, J. D.; Nickias, P. N.; Selegue, J. P. *Inorg. Chem.* **1987**, *26*, 3424.
- (21) Erker, G.; Petrenz, R.; Krüger C.; Lutz, F.; Weiss, A.; Werner, S. *Organometallics* **1992**, *11*, 1646.
- (22) Benson, J. W.; Angelici, R. J. *Inorg. Chem.* **1993**, *32*, 1871.

- (23) Abel, E. W.; Orrell, K. G.; Bhargava, S. K. *Prog. Inorg. Chem.* **1984**, 32, 1.
- (24) Östman, B.; Olsson, S. *Arkiv. Kem.* **1960**, 15, 275.
- (25) Scrowston, R. M. *Adv. Heterocycl. Chem.* **1981**, 29, 171, and references therein.
- (26) Peng, T.-S.; Gladysz, J. A. *Organometallics* **1990**, 9, 2884.
- (27) Kowalczyk, J. J.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1991**, 124, 729.
- (28) *CRC Handbook of Chemistry and Physics*, Weast, R. C., ed.; CRC Press, Inc.: Boca Raton, 1984.
- (29) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, 110, 6110.
- (30) McCormick, F. B.; Gladysz, J. A. *J. Organomet. Chem.* **1981**, 218, C57.
- (31) Hatton, W. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, 105, 6157.
- (32) (a) Yu, Y. S.; Angelici, R. J. *Organometallics* **1983**, 2, 1018. (b) Yu, Y. S.; Angelici, R. J. *Organometallics* **1983**, 2, 1583. (c) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1980**, 102, 2455. (d) Casey, C. P.; Polichnowski, S. W.; Schusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, 101, 7282.
- (33) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, 105, 305.
- (34) Agbossou, S. K.; Bodner, G. S.; Patton, A. T.; Gladysz, J. A. *Organometallics* **1990**, 9, 1184.
- (35) (a) Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, 6, 1146. (b) Spies, G. H.; Angelici, R. J. *J. Am. Chem. Soc.* **1985**, 107, 5569.

- (36) Lopez, L.; Godziela, G.; Rakowski Dubois, M. *Organometallics* **1991**, *10*, 2660.
- (37) Cowley, S. W., Ph.D. Dissertation, Southern Illinois University, 1975.
- (38) Hockett, S. C.; Angelici, R. J.; Ekman, M. E.; Schrader, G. L. *J. Catal.* **1988**, *113*, 36.

**PAPER 3. ADSORPTION OF ARYL AND ALKYL ISOCYANIDES
ON POWDERED GOLD¹**

ABSTRACT

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is used to examine the adsorption of phenylisocyanide (PhNC), *t*-butylisocyanide (Bu^tNC), and 1,4-phenylene diisocyanide (1,4-DINC) from methanol solution on gold powder. These studies indicate that the isocyanides bond end-on to a single gold atom through the terminal carbon atom of the isocyanide group. This structural assignment is based on a comparison of the $\nu(\text{NC})$ values of the isocyanides adsorbed on gold with those in (PhNC)AuCl, (Bu^tNC)AuCl, and isocyanide gold cluster compounds. The $\nu(\text{NC})$ frequencies of the isocyanides typically shift 50-70 cm⁻¹ higher upon adsorption to the gold powder when compared to the uncoordinated isocyanides. The spectra indicate that 1,4-DINC coordinates only one isocyanide group to the gold; the other one remains uncoordinated. When the concentration of the isocyanide in the methanol is increased, the amount of isocyanide adsorbed increases up to a limiting value of approximately one RNC per surface Au atom for PhNC and 1,4-DINC. The limiting value for Bu^tNC is about 0.3 RNC per surface Au. The steric bulk of the Bu^t group may reduce the number of Bu^tNC molecules that can be packed onto the surface. At all loadings, the isocyanides bind to only one Au atom; there is no evidence for bridging RNC groups.

INTRODUCTION

Carbon monoxide (CO) and alkyl and aryl isocyanides (CN-R) are isoelectronic and form numerous transition metal complexes.² Considerable evidence indicates that the CO ligand is a better π acceptor of electron density from the metal than isocyanides, but isocyanides may be stronger σ donors than CO.³ While the coordination chemistry of both of these ligands in organometallic complexes has been widely studied, only CO has been extensively studied as a ligand on many metal surfaces.⁴ In contrast, relatively little is known about the adsorption of isocyanides on metal surfaces.⁵ Methyl isocyanide (CH₃NC), the simplest alkyl isocyanide, has been examined on several metal faces. On Ni(100)^{5a,b} and Ni(111),^{5c} the CH₃NC binds strongly to the surface, and it is proposed that the N-C bond of the isocyanide group lies parallel to the surface. On Rh(111),^{5d} the isocyanide binds strongly to the surface as a bridged species, most likely involving both the carbon and nitrogen atoms of the isocyanide group. However, on supported rhodium, Rh/Al₂O₃,^{5e} CH₃NC binds to the rhodium presumably in an end-on fashion to one surface atom through the terminal carbon of the isocyanide group. On Pt(111)^{5f}, CH₃NC binds terminally at all coverages, but there is also evidence for isocyanide bonding to two or more atoms at higher coverages. On the other hand, CH₃NC binds parallel to the surface on Ag(311) at lower coverages, and only terminal, upright bonding is observed at higher coverages. Ethyl isocyanide (CH₃CH₂NC) adsorption on Fe, Co, Ni, Rh, Pd, and Pt

evaporated films has also been reported,^{5h} and only terminal bonding of the isocyanide was observed.

Relatively little is known about adsorption on gold surfaces because so few molecules chemisorb on this metal. Gold is inert and resistant to oxidation; O₂ only adsorbs molecularly at low temperatures on clean gold surfaces, and no surface oxide forms.⁶ Molecules such as water⁷ and ethylene^{7a,8} also do not chemisorb or bind appreciably to gold surfaces. On the other hand, alkanethiols (RSH) and disulfides (RSSR) adsorb strongly on gold films; these systems have been studied extensively.⁹ Many infrared spectroscopic investigations of the adsorption of CO on gold surfaces have been reported,¹⁰ with several involving infrared analysis.^{10a-g} In all of these cases, the CO is proposed to bond terminally to one Au atom. Adsorption of the isocyanide, tricosylisonitrile (CH₃(CH₂)₂₂NC), to a gold surface has been mentioned briefly,¹¹ but to our knowledge, no other studies of isocyanides on gold surfaces have been published.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is a technique that has been used widely to study the adsorption of a variety of molecules on solid surfaces.¹² With this technique, the radiation penetrates into a powder or solid and is reflected, refracted and diffracted at particle boundaries and interfaces,^{12a} In the investigations reported in this paper, it is the $\nu(\text{NC})$ absorption of the adsorbed isocyanides (RNC) that is most useful for assigning the mode of isocyanide coordination to the surface. The

$\nu(\text{NC})$ vibration is also used to assign bonding modes in transition metal complexes with isocyanide ligands.²

With the long range goal of investigating reactions of aryl and alkyl isocyanides on metal surfaces, we begin with the current DRIFTS studies of the adsorption of phenyl isocyanide (PhNC), *t*-butylisocyanide (Bu^tNC), and 1,4-phenylene diisocyanide (1,4-DINC) on gold

powder. The results show that both aryl and alkyl isocyanides do indeed chemisorb to Au, and the $\nu(\text{NC})$ vibrational frequencies allow the mode of adsorption to be assigned by comparison with $\nu(\text{NC})$ values in transition metal complexes.

EXPERIMENTAL

PhNC was prepared by a literature method¹³ and distilled immediately before use. 1,4-DINC and Bu^tNC were purchased from Aldrich; Bu^tNC was used as received, and 1,4-DINC was sublimed under vacuum with gentle heating prior to use. Methanol was dried and distilled over Mg/I₂¹⁴ and stored under N₂. (PhNC)AuCl and (Bu^tNC)AuCl were prepared by literature methods¹⁵ from (Me₂S)AuCl.¹⁶

The gold powder was prepared from HAuCl₄ by reduction with hydroquinone according to a published procedure.¹⁷ The gold powder was washed with MeOH in a Soxhlet extractor for 24 h or until the MeOH ran colorless through the extraction thimble. The powder was then ground with mortar and pestle and dried for an hour in a oven at 110° C. There was no evidence for adsorption of organic impurities on the powder as determined by a DRIFT spectrum of the powder when ratioed to mirror, KBr, and PdCl₂ backgrounds; no C-H stretching frequencies were observed in the region 3200-2800 cm⁻¹, and no bands were present at lower wavenumbers. An XPS spectrum of the powder was recorded on a AEI 200B spectrometer. Routine BET surface area measurements were performed on a Micromeritics AccuSorb 2100E instrument. Using Kr as the adsorbate gas at 88 K, the surface area of the gold powder was determined to be 0.35 m²/g. Electron micrographs of the Au powder were recorded on a JEOL JSM scanning microscope. The gold powder was deposited on an aluminum foil background from a suspension in diethyl ether.

FT-IR and DRIFT Spectroscopy. All infrared spectra were recorded on a Nicolet 710 spectrophotometer equipped with a TGS detector in the main compartment and an MCT detector in the auxiliary experiment module (AEM). The AEM housed a Harrick diffuse reflectance accessory. The spectrometer was modified by Nicolet Instrument Corporation at the factory so that 340 scans/min could be collected at 4 cm^{-1} resolution using the MCT detector. The instrument was continuously purged with nitrogen gas. All DRIFT spectra were recorded with the samples in the Harrick microsampling cup. The background used for DRIFT spectra was clean gold powder. Spectra were routinely baseline corrected and purge corrected. The spectra were recorded and reported with absorbance units as the abscissa, even though the radiation collected is actually reflectance. Kubelka-Munk transformation of the spectra was not possible due to the low intensity of all bands; the bands were eliminated by the transformation. The pseudo-absorbance units used do appear to behave according to Beer's Law (vide infra). However, fully quantitative measurements may not always be possible using DRIFTS.^{12a}

Sample Preparation. Stock solutions of the aryl or alkyl isocyanides were prepared in 10.00 mL of MeOH using the following quantities: PhNC, $2.0\text{ }\mu\text{ L}$ ($1.9 \times 10^{-5}\text{ mol}$); Bu^tNC, $2.0\text{ }\mu\text{ L}$ ($1.8 \times 10^{-5}\text{ mol}$); 1,4-DINC, 0.0020 g ($1.6 \times 10^{-5}\text{ mol}$). Samples of isocyanide adsorbed on gold powder were prepared in air in the following manner: 1) 0.050 g of Au powder was placed in a test tube; 2) 0.5 mL of MeOH was added; 3) the appropriate amount of isocyanide stock solution ($0.5\text{ }\mu\text{ L}$ - 600

μL) was added, followed by addition of another 0.5 mL of MeOH; 4) the test tube was shaken for 30 s using a Genie vortex mixer and then centrifuged; 5) the liquid was decanted, and the gold powder was dried under oil pump vacuum (typically 10 min.); 6) the powder was poured into the microsampling cup for infrared analysis and leveled by gently tapping the sample cup.

RESULTS AND DISCUSSION

Powdered Gold. The gold powder was synthesized¹⁷ by reduction of HAuCl_4 with hydroquinone in aqueous solution (eq 1), washed

thoroughly with MeOH, and dried at 110 °C. An XPS spectrum of the powder showed that the sample was pure Au(0), as evidenced by the sharp lines for the Au 4f_{5/2} and Au 4f_{7/2} binding energies at 88.0 and 84.8 eV, as well as other characteristic but less intense lines for other levels of Au(0).¹⁸ No Au(I) was detected, and no lines were observed for any impurities, like chlorine or oxygen species, that could be plausible contaminants in the powder. A DRIFT spectrum of the powder when ratioed to various backgrounds showed no C-H stretching frequencies in the region 3200-2800 cm⁻¹ and no other observable bands at lower wavenumbers, indicating that no hydroquinone reactant or quinone product was adsorbed on the surface. The spectrum also indicated that the MeOH and H₂O solvents did not adhere to the surface either. H₂O⁷ and MeOH¹⁹ were previously observed in UHV studies not to adsorb on clean gold surfaces, except molecularly at low temperatures.

Electron micrographs of the gold powder were recorded at several magnifications. At 3000x magnification, it appears that the powder is

made up of aggregates of small gold particles relatively uniform in size that are melded together (Figure 1). Closer examination of these particles at magnification 30000x (Figure 2) shows that these particles appear to be solid and nonporous. They actually seem to be made up of many small spheres of gold packed together, as evidenced by the boundary lines on the surface of the particles. Aggregated gold particles are often observed in gold powders precipitated from aqueous solution, but the size of the particles and degree of aggregation may depend on the type of reductant used.²⁰

The measured surface area ($0.35 \text{ m}^2/\text{g}$) was used to estimate the number of gold atoms that would be present on the surface of the gold powder and act as coordination sites for the isocyanides. Given that gold metal has a cubic close-packed structure with unit cell edge length $a = 4.078 \text{ \AA}$,²¹ the area of one unit cell face (the (100) face) is $16.63 \text{ \AA}^2$ ($1.663 \times 10^{-19} \text{ m}^2$). This face has two surface gold atoms (one in the center of the face and one fourth of an atom at each corner). Thus, there are $2 \text{ Au atoms}/16.63 \text{ \AA}^2$, or $1.2 \times 10^{19} \text{ Au atoms}/\text{m}^2$ or $2.0 \times 10^{-5} \text{ mol Au atoms}/\text{m}^2$. Using the measured surface area of the Au powder ($0.35 \text{ m}^2/\text{g}$), one calculates $7.0 \times 10^{-6} \text{ mol Au atoms}$ present on the surface of the powder for every one gram of Au, $7.0 \times 10^{-6} \text{ mol Au}_{(\text{surf})}/\text{g Au}$. In other words, there is roughly 1 surface Au atom for every 725 Au atoms total. This calculation assumes the surface of the Au powder to have a (100) structure ($2 \text{ Au}_{(\text{surf})} \text{ atoms}/16.63 \text{ \AA}^2$). A similar calculation for the (110) and (111) surfaces shows that there

Figure 1. Electron micrograph of Au powder, 3000X magnification

Figure 2. Electron micrograph of Au powder, 30000X magnification

are 1.4 and 2.4 $\text{Au}_{(\text{surf})}$ atoms/ $16.63 \text{ \AA}^2$, respectively. Therefore, for the polycrystalline powder used in these studies, 2 $\text{Au}_{(\text{surf})}$ atoms/ $16.63 \text{ \AA}^2$ is a reasonable estimate of the number of Au atoms on the surface of the powder.

Adsorption of Isocyanides on Powdered Gold. The isocyanides were adsorbed on 0.050 g of Au powder from MeOH solution. The value of $7.0 \times 10^{-6} \text{ mol Au}_{(\text{surf})}/\text{g Au}$ was used to calculate the amount of isocyanide used in solution for the adsorptions. For example, for a 0.034 ratio of isocyanide to surface Au atoms in 0.050 g of powder, the volume of isocyanide stock solution equivalent to $(0.034)(0.050\text{g})(7.0 \times 10^{-6} \text{ mol/g}) = 1.2 \times 10^{-8} \text{ mol}$ of isocyanide was used.

Spectra of each isocyanide, Bu^tNC , PhNC , and 1,4-DINC, adsorbed on gold using a 0.034 ratio of moles of isocyanide in solution to moles of gold surface atoms are shown in Figure 3. The bands are not intense, roughly 0.0030-0.0050 absorbance units. A comparison of the $\nu(\text{NC})$ values for the uncoordinated isocyanides in CH_2Cl_2 solution and for the isocyanides adsorbed on Au is given in Table I. The $\nu(\text{NC})$ values shift 50-70 cm^{-1} higher upon adsorption to the gold powder.

The high $\nu(\text{NC})$ values for the isocyanides adsorbed on the gold powder are characteristic of terminal RNC ligands in organometallic complexes in which the carbon of the isocyanide ligand is bonded to one metal atom.² Isocyanides are also known to bridge two or three metal atoms in transition metal cluster complexes.² However, $\nu(\text{NC})$ values for bridging isocyanide ligands in these complexes are in the range

Figure 3. DRIFT spectra of $\nu(\text{NC})$, cm^{-1} , for ButNC, PhNC, and 1,4-DINC adsorbed on powdered Au; 0.034 mol RNC used/mol $\text{Au}_{(\text{surf})}$.

Table I. $\nu(\text{NC})$ frequencies for R-NC, cm^{-1}

	in CH_2Cl_2 solution	adsorbed on Au	$(\text{R-NC})\text{AuCl}^a$
PhNC	2130	2190	2228
Bu^tNC	2134	2208	2241
1,4-DINC	2128	2180(s) ^b , 2121(vs) ^c	

^aIn acetone ^bCoordinated to surface ^cUncoordinated

1800-1570 cm^{-1} . Since no bands were observed in this region for the isocyanides adsorbed on gold powder at all loadings used, there is no evidence for any type of bridging isocyanide in this system. It should be noted, however, that this spectral region is somewhat obscured by weak bands of adventitious water vapor. The $\nu(\text{NC})$ absorbance intensity of a 0.034 mol PhNC/mol $\text{Au}_{(\text{surf})}$ sample was not diminished when washed with 2 mL of MeOH for 30 s and recording the spectrum of the gold powder as usual.

The organometallic complexes $(\text{RNC})\text{AuCl}$, $\text{R} = \text{Ph}$ or Bu^t , were synthesized¹⁵ as models for the adsorption of isocyanides on gold powder. In all of the complexes, the oxidation state of the gold is formally +1. A comparison of $\nu(\text{NC})$ values for the free isocyanides and coordinated isocyanides in the $(\text{RNC})\text{AuCl}$ compounds (Table I) shows that $\nu(\text{NC})$ is approximately 100 cm^{-1} higher in the Au(I) complexes. This increase in $\nu(\text{NC})$ suggests that there is relatively little π backbonding from the Au(I) to the RNC ligands. In contrast, the $\nu(\text{C}\equiv\text{N})$ bands of PhNC and Bu^tNC adsorbed on Au powder are only 60 and 74 cm^{-1}

¹ higher than the free RNC. The lower $\nu(\text{NC})$ values for the isocyanides on Au are consistent with the lower oxidation state of Au metal as compared with that in the Au(I) complexes. The $\nu(\text{NC})$ value of Bu^tNC adsorbed on Au powder (2208 cm^{-1}) is slightly higher than values reported for the gold clusters $\text{Au}_8(\text{PPh}_3)_7(\text{CNBu}^t)_2^{2+}$ (2186 cm^{-1}) and $\text{Au}_9(\text{PPh}_3)_6(\text{CNBu}^t)_2^{3+}$ (2175 cm^{-1}).²² The Bu^tNC groups are bonded as terminal ligands to peripheral gold atoms in each of the clusters.

The spectrum of 1,4-DINC on powdered gold (Fig. 3) is particularly interesting because it shows both coordinated and uncoordinated NC groups. In free 1,4-DINC, both NC groups are equivalent, and only one $\nu(\text{NC})$ band is observed in solution (2128 cm^{-1}). When adsorbed on gold (Fig. 3, Table I), 1,4-DINC shows one $\nu(\text{NC})$ band (2180 cm^{-1}) at a position 52 cm^{-1} higher than that of the uncoordinated 1,4-DINC. The position of this band is similar to that (2190 cm^{-1}) of PhNC adsorbed on gold; broadening of the 2180 cm^{-1} band is presumably due to the inhomogeneity of the surface adsorption sites. Another band at 2121 cm^{-1} in the spectrum of 1,4-DINC on Au is much sharper and more intense than the coordinated $\nu(\text{NC})$ adsorption. It is shifted only 7 cm^{-1} lower than that of free 1,4-DINC and can be assigned to an uncoordinated NC group. Considering the structure of 1,4-DINC, it is sterically impossible for both isocyanide groups to coordinate end-on to the surface, unless the molecule bridges a pore or a gap on the surface, which seems unlikely based on the structure of the solid (Figs. 1-2). Thus, it appears that 1,4-DINC, like PhNC and

ButNC, coordinates through one NC group as a terminal ligand to one Au atom on the surface.

Attempts to synthesize the complex (1,4-DINC)AuCl, in which only one NC group is coordinated, were unsuccessful. The insoluble tan solid obtained from the reaction of (Me₂S)AuCl with 1,4-DINC showed evidence of only coordinated NC groups (2234 cm⁻¹ in Nujol mull). Attempts to synthesize the reported complexes W(CO)₅(1,4-DINC)²³ and (CO)₄(Br)Mn(1,4-DINC),²⁴ in which only one end of the 1,4-DINC is coordinated were unsuccessful. Insoluble solids were obtained, and infrared spectra of the solids in Nujol mulls did not show ν(NC) bands for uncoordinated NC groups.

Varying the Amount of Adsorbed RNC. Increasing the amount of RNC in the MeOH solution increased the amount of RNC adsorbed on the surface (Table II). This increased adsorption was measured by the

absorbance of the $\nu(\text{NC})$ band at the peak maximum. To insure accuracy and to circumvent any reflectance irregularities in a specific sample spectrum, at least three spectra were recorded for each sample. For each spectrum, the gold powder was removed from the microsampling cup and reloaded. The intensities of the $\nu(\text{NC})$ bands reported in Table II are the average intensities of the $\nu(\text{NC})$ bands in these spectra. For example, the intensities of the $\nu(\text{NC})$ band in three spectra of the PhNC sample using a 0.034 ratio of PhNC to surface gold atoms were 0.0049, 0.0049, and 0.0050, to give an average intensity of 0.0049. The spectrum for a given sample is reproducible if another sample is prepared independently in the same manner. For all loadings used, the $\nu(\text{NC})$ band position maximum did not vary within 4 cm^{-1} ; the average band positions are given in Table I. For both adsorbed PhNC and Bu^tNC at all loading levels, only one $\nu(\text{NC})$ band was observed; there was no evidence for bridging RNC groups that would be expected to exhibit $\nu(\text{NC})$ bands in the $1800\text{--}1570\text{ cm}^{-1}$ region.²

Figure 4 shows the $\nu(\text{NC})$ band of Bu^tNC adsorbed on Au increasing in intensity with increasing amounts of isocyanide used in the methanol solution. Plots of the intensities of the $\nu(\text{NC})$ bands with varying amounts of PhNC, Bu^tNC, and 1,4-DINC used are presented in Figures 5 and 6, respectively. With PhNC and 1,4 DINC, the $\nu(\text{NC})$ band reaches a maximum intensity at about a 1:1 ratio of isocyanide used to surface gold atoms. This fact would seem to indicate that the surface of the gold powder is saturated with isocyanide at this point; in other words, all of the gold atoms on the surface of the gold powder are

Table II. $\nu(\text{NC})$ band intensities of RNC adsorbed on Au powder
as determined by DRIFTS

moles of RNC used in solution	ratio ^a RNC: Au _(surf)	PhNC 2190 cm ⁻¹	Bu ^t NC 2208 cm ⁻¹	1,4-DINC 2180 / 2121 cm ⁻¹
1.4x10 ⁻⁹	0.0040	0.0018	0.0012	0.0007/ 0.0009
2.9x10 ⁻⁹	0.0083	0.0029	0.0013	0.0008/ 0.0013
5.8x10 ⁻⁹	0.017	0.0050	0.0022	0.0019/ 0.0032
1.2x10 ⁻⁸	0.034	0.0049	0.0025	0.0024/ 0.0046
2.4x10 ⁻⁸	0.067	0.0059	0.0029	0.0034/ 0.0054
3.6x10 ⁻⁸	0.10	0.0064		0.0041/ 0.0072
6.0x10 ⁻⁸	0.17	0.0073	0.0040	0.0050/ 0.0085
1.2x10 ⁻⁷	0.34	0.0091	0.0046	0.0063/ 0.0110
3.0x10 ⁻⁷	0.85	0.0105	0.0046	0.0080/ 0.0127
6x10 ⁻⁷	1.7	0.0106	0.0044	0.0088/ 0.0121

^aSee text for method of estimating mol Au_(surf)

Figure 4. DRIFT spectra of $\nu(\text{NC})$, cm^{-1} , for ButNC adsorbed on powdered Au with increasing ratios of mol ButNC used in MeOH solution/mol Au(surf)

Figure 5. $\nu(\text{NC})$ intensities of $\text{Bu}^{\text{t}}\text{NC}$ and PhNC adsorbed on powdered Au with increasing amounts of RNC in MeOH solution. See text for method of estimating $\text{mol Au}_{(\text{surf})}$

Figure 6. $\nu(NC)$ intensities of 1,4-DINC adsorbed on powdered Au with increasing amounts of RNC in MeOH solution. See text for method of estimating mol $Au_{(surf)}$

coordinated to an isocyanide. This idea is supported by the fact that at the highest ratio (1.7:1), PhNC can be detected in the MeOH solution that is decanted from the gold powder after adsorption. This is done by evaporating the solution to dryness and measuring the FT-IR spectrum of the residue in CH₂Cl₂. Because of the very small amounts involved, it was not possible for us to quantitatively detect the isocyanide concentration in the decanted solution, nor could the isocyanide be detected in solutions at lower ratios by conventional means such as UV-VIS, NMR or infrared techniques. For Bu^tNC, the maximum $\nu(\text{NC})$ intensity is reached at about the 0.3:1 ratio of Bu^tNC used to Au_(surf) atoms, not at the 1:1 ratio as for the PhNC and 1,4-DINC. Perhaps the bulkiness of the Bu^t group prevents adsorption on all surface atoms.

CONCLUSION

DRIFTS was used successfully to observe PhNC and Bu^tNC adsorbed on gold powder from methanol solution. Spectra of the dosed samples indicate that the isocyanides are coordinated end-on to one Au atom through the carbon atom of the isocyanide functionality. For the 1,4-phenylene diisocyanide (1,4-DINC), only one of the NC groups coordinates to the surface, while the other remains uncoordinated. The $\nu(\text{NC})$ band intensities of the adsorbed isocyanides increase with the amount of isocyanide used; eventually these intensities reach a limiting value, which suggests that the surface is saturated with the isocyanide. For PhNC and 1,4-DINC, the maximum intensity is reached when the moles of isocyanide used is approximately equal to the estimated moles of gold atoms on the surface of the powder; thus, it appears that the unit cell dimensions for gold and the surface area of the powder can be used to approximate the number of adsorption sites on the surface of the gold powder. However, using Bu^tNC, the maximum intensity is reached at approximately a 0.3:1 ratio of isocyanide used to surface gold atoms. It appears that steric effects of the bulky Bu^t group inhibits adsorption to all surface Au atoms.

Acknowledgments. We thank Jim Anderegg for recording the XPS spectrum and Mitch Meyer for performing electron microscopy on the gold powder.

REFERENCES

- (1) Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division.
- (2) a) Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 193. b) Treichel, P. M. *Adv. Organomet. Chem.* **1973**, *11*, 121. c) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 130. d) Crociani, B. in *Reactions of Coordinated Ligands*, vol. 1, P. S. Braterman, ed., Plenum Press: New York, 1986. e) Malatesta, L.; Bonati, F. *Isocyanide Complexes of Metals*, Wiley Interscience: London, 1969.
- (3) Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* **1975**, *14*, 247.
- (4) a) Hoffman, F. M. *Surf. Sci. Rep.* **1983**, *3*, 1, and references therein. b) Vuckovic, D. L.; Jansen, S. A.; Hoffmann, R. *Langmuir* **1990**, *6*, 732.
- (5) a) Friend, C. M.; Stein, J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 767. b) Hemminger, J. C.; Muetterties, E. L.; Somorjai, G. A. *J. Am. Chem. Soc.* **1972**, *101*, 62. c) Friend, C. M.; Muetterties, E. L.; Gland J. L. *J. Phys. Chem.* **1981**, *85*, 3256. d) Semancik, S.; Haller, G. L.; Yates, Jr., J. T. *J. Chem. Phys.* **1983**, *78*, 6970. e) Cavanagh, R. R.; Yates, Jr., J. T. *J. Chem. Phys.* **1981**, *75*, 1551. f) Avery, N. R.; Matheson, T. W. *Surf. Sci.* **1984**, *143*, 110. g) Ceyer, S. T.; Yates, Jr., J. T. *J. Phys. Chem.* **1985**, *89*, 3842. h) Queau, R.; Poilblanc, R. *J. Catal* **1972**, *27*, 200.

- (6) a) Pireaux, J. J.; Chtaïb, M.; Delrue, J. P.; Thiry, P. A.; Liehr, M.; Caudano, R. *Surf. Sci.* **1984**, *141*, 211. b) Canning, N. D. S.; Outka, D.; Madix, R. J. *Surf. Sci.* **1984**, *141*, 240. c) Sault, A. G.; Madix, R. J.; Campbell, C. T. *Surf. Sci.* **1986**, *169*, 347.
- (7) a) Chesters, M. A.; Somorjai, G. A. *Surf. Sci.* **1975**, *52*, 21. b) Schrader, M. E. *J. Colloid Interface Sci.* **1977**, *59*, 456. c) Wells, R. L.; Fort, Jr., T. *Surf. Sci.* **1972**, *32*, 554. d) Brundle, C. R.; Roberts, M. W. *Surf. Sci.* **1973**, *38*, 234. e) Kay, B. D.; Lykke, K. R.; Creighton, J. R.; Ward, S. J. *J. Chem. Phys.* **1989**, *91*, 5120.
- (8) a) Franken, P. E. C.; Ponec, V. *Surf. Sci.* **1975**, *53*, 341. b) Outka, D. A.; Madix, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 1708.
- (9) a) Ulman, A. *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly*, Academic Press, Inc.: New York, 1991. b) Whitesides, G. M.; Laibinis, P. E. *Langmuir* **1990**, *6*, 87. c) Alves, C. A.; Smith, E. L. Porter, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 1222. d) Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 1990. e) Weisshaar, D. E.; Lamp, B. D.; Porter, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 5860. f) Ong, T. H.; Ward, R. N.; Davies, P. B.; Bain, C. D. *J. Am. Chem. Soc.* **1992**, *114*, 6243.
- (10) a) Kavtaradze, N. N.; Sokolova, N. P. *Russ. J. Phys. Chem.* **1962**, *36*, 1529. b) Guerra, C. R.; Schulman, J. H. *Surf. Sci.* **1967**, *7*, 229. c) Guerra, C. R. *Colloid Interface Sci.* **1969**, *29*, 229. d) Yates, D. J. C. *Colloid Interface Sci.* **1969**, *29*, 197. e) Bradshaw, A. M.; Pritchard, J. *Proc. Roy. Soc. (London) A* **1970**, *316*, 169. f) Kottke, M. L.; Greenler, R. G.; Tompkins, H. G. *Surf. Sci.* **1972**, *32*,

231. g) Dumas, P.; Tobin, R. G.; Richards, P. L. *Surf. Sci.* **1986**, *171*, 579. h) Takasu, Y.; Yasuda, K.; Matsuda, Y.; Toyoshima, I. *Chem. Phys. Lett.* **1988**, *152*, 105. i) Norton, P. R.; Tapping, R. L.; Goodale, J. W. *Surf. Sci.* **1978**, *72*, 33. j) Surplice, N. A.; Brearley, W. *Surf. Sci.* **1975**, *52*, 62. k) McElhiney, G.; Pritchard, J. *Surf. Sci.* **1976**, *60*, 397. l) Outka, D. A.; Madix, R. J. *Surf. Sci.* **1987**, *179*, 351.
- (11) Bain, C. D.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7155.
- (12) a) *Advances in Applied Fourier Transform Infrared Spectroscopy* M. W. Mackenzie, ed.; John Wiley & Sons: New York, 1988. b) Fuller, M. P.; Griffiths, P. R. *Appl. Spectrosc.* **1980**, *34*, 5. c) Venter, J. J.; Vannice, M. A. *Carbon* **1988**, *26*, 889.
- (13) Weber, W. P.; Gokel, G. W.; Ugi, I. K. *Angew. Chem. Int. Ed. Engl.*, **1972**, *11*, 530.
- (14) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1980.
- (15) a) McCleverty, J. A.; da Mota, M. M. M.; *J. Chem. Soc. Dalton Trans.* **1973**, 2571.
- (16) Phillips, F. C. *J. Am. Chem. Soc.* **1901**, *23*, 257.
- (17) Block, B. P. *Inorg. Synth.* **1953**, *4*, 14.
- (18) Prutton, M. *Surface Physics*, 2nd edition, Oxford University Press: Oxford, 1983, and references therein.
- (19) Outka, D. A.; Madix, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 1708.
- (20) Collier, N. *Gold Bulletin* **1977**, *10*, 62.

- (21) Wyckoff, R.W.G. *Crystal Structures*, 2nd ed., vol. 1; Interscience Publishers: New York, 1963.
- (22) a) Bos, W.; Kanters, R. P. F.; van Halen, C. J.; Bosman, W. P.; Behm, H.; Smits, J. M. M.; Beurskens, P. T.; Bour, J. J. *J. Organomet. Chem.* **1986**, 307, 385. b) Bos, W.; van der Velden, J. W. A.; Steggerda, J. J.; Casalnuovo, A. L.; Pignolet, L. H. *J. Organomet. Chem.* **1983**, 253, C64.
- (23) Grubisha, D. S.; Rommel, J. S.; Lane, T. M.; Tysoe, W. T.; Bennett, D. W. *Inorg. Chem.* **1991**, 31, 5022.
- (24) Efraty, A.; Feinstein, I.; Wackerle, L. *J. Organomet. Chem.* **1981**, 220, 333.

GENERAL SUMMARY

My research has shown that organometallic rhenium complexes can be synthesized that contain a sulfur-coordinated thiophene (T) or benzothiophene (BT). Sulfur coordination of these thiophenes have activated them to undergo reactions with acids and/or bases. In one case, $\text{Cp}'(\text{CO})_2(\eta^1(\text{S})\text{-BT})$ reacts with acid to form the bimetallic complexes $[\text{Cp}'(\text{CO})_2\text{Re}](\eta^2:\eta^1(\text{S})\text{-}\mu_2\text{-BT})$. The dual metal coordination to the BT actually appears to enhance the donating ability of the sulfur atom in the BT. In the $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{thiophene})^+$ complexes, sulfur coordination makes the hydrogens on the thiophene more acidic. The thiophenes can be deprotonated to give the neutral thienyl complexes, and these thienyl complexes can be protonated to give the novel thienylcarbene complexes.

Another aspect of my research has shown that diffuse reflectance infrared Fourier transform spectroscopy can be used to observe alkyl and aryl isocyanides adsorbed on the surface of gold powder. The $\nu(\text{NC})$ frequencies were compared to homogeneous compounds to determine the bonding mode of the isocyanides. The isocyanides all bonded through the terminal carbon of the isocyanide group to one gold atom on the surface. The number of gold atoms on the surface that could act as possible adsorption sites was estimated from the surface area of the gold powder and the dimensions of a unit cell face of gold metal. With PhNC and 1,4-DINC, the $\nu(\text{NC})$ intensity reached a maximum value at approximately a 1:1 ratio of moles of isocyanide used to the moles of estimated gold atoms on the surface of the powder. Thus, it appears

possible to estimate the number of surface adsorption sites on a solid based on its surface area and the unit cell dimensions of the solid compound itself. These studies show that it is possible to further examine the adsorption and reaction of isocyanides on gold surfaces.

This work was performed at Ames Laboratory under contract number W-7405-Eng-82 with the U. S. Department of Energy. This dissertation has been assigned the DOE Report number IS-T 1645.

ADDITIONAL REFERENCES

1. Adamson, A. W. *Physical Chemistry of Surfaces*, 4th ed.; John Wiley & Sons: New York, 1982.
2. Kavtaradze, N. N.; Sokolova, N. P. *Russian J. Phys. Chem.* **1962**, *36*, 1529.
3. Guerra, C. R.; Schulman, J. H. *Surf. Sci.* **1967**, *7*, 229.
4. Guerra, C. R. *Colloid Interface Sci.* **1969**, *29*, 229.
5. Yates, D. J. C. *Colloid Interface Sci.* **1969**, *29*, 197.
6. Bradshaw, A. M.; Pritchard, J. *Proc. Roy. Soc. (London) A* **1970**, *316*, 169.
7. Kottke, M. L.; Greenler, R. G.; Tompkins, H. G. *Surf. Sci.* **1972**, *32*, 231.
8. Dumas, P.; Tobin, R. G.; Richards, P. L. *Surf. Sci.* **1986**, *171*, 579.
9. Takasu, Y.; Yasuda, K.; Matsuda, Y.; Toyoshima, I. *Chem. Phys. Lett.* **1988**, *152*, 105.
10. Norton, P. R.; Tapping, R. L.; Goodale, J. W. *Surf. Sci.* **1978**, *72*, 33.
11. Surplice, N. A.; Brearley, W. *Surf. Sci.* **1975**, *52*, 62.
12. McElhiney, G.; Pritchard, J. *Surf. Sci.* **1976**, *60*, 397.
13. Outka, D. A.; Madix, R. J. *Surf. Sci.* **1987**, *179*, 351.
14. Bowker, M. Barteau, M. A.; Madix, R. J. *Surf. Sci.* **1980**, *92*, 528.
15. Eley, D. D.; Moore, P. B. *Surf. Sci.* **1978**, *76*, L599.
16. Chesters, M. A.; Somorjai, G. A. *Surf. Sci.* **1975**, *52*, 21.
17. Schrader, M. E. *J. Colloid Interface Sci.* **1977**, *59*, 456.
18. Schrader, M. E. *Surf. Sci.* **1978**, *78*, L227.
19. Légaré, P.; Hilaire, L.; Sotto, M.; Maire, G. *Surf. Sci.* **1980**, *91*, 175.

20. Pireaux, J. J.; Chtaïb, M.; Delrue, J. P.; Thiry, P. A.; Liehr, M.; Caudano, R. *Surf. Sci.* **1984**, *141*, 211.
21. Canning, N. D. S.; Outka, D.; Madix, R. J. *Surf. Sci.* **1984**, *141*, 240.
22. Sault, A. G.; Madix, R. J.; Campbell, C. T. *Surf. Sci.* **1986**, *169*, 347.
23. Wells, R. L.; Fort, Jr., T. *Surf. Sci.* **1972**, *32*, 554.
24. Brundle, C. R.; Roberts, M. W. *Surf. Sci.* **1973**, *38*, 234.
25. Kay, B. D.; Lykke, K. R.; Creighton, J. R.; Ward, S. J. *J. Chem. Phys.* **1989**, *91*, 5120.
26. Kostelitz, M.; Domange, J. L.; Oudar, J. *Surf. Sci.* **1973**, *34*, 431.
27. Jaffey, D. M.; Madix, R. J. *Surf. Sci.* **1991**, *258*, 359.
28. Chtaïb, M.; Thiry, P. A.; Pireaux, J. J.; Delrue, J. P.; Caudano, R. *J. Electro. Spec. Related Phen.* **1983**, *29*, 293.31.
29. Chtaïb, M.; Thiry, P. A.; Pireaux, J. J.; Delrue, J. P.; Caudano, R. *Surf. Sci.* **1985**, *162*, 245.
30. Outka, D. A.; Madix, R. J. *Surf. Sci.* **1987**, *179*, 361.
31. Outka, D. A.; Madix, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 1708.
32. Kishi, K.; Ikeda, S. *J. Phys. Chem.* **1974**, *78*, 107.
33. Spencer, N. D.; Lambert, R. M. *Surf. Sci.* **1981**, *107*, 237.
34. Sesselmann, W.; Marinero, E. E.; Chuang, T. J. *Surf. Sci.* **1986**, *178*, 787.
35. Netzer, F. P.; Bertel, E.; Matthew, J. A. D. *Solid State Comm.* **1980**, *33*, 519.
36. Cochran, S. A.; Farrell, H. H. *Surf. Sci.* **1980**, *95*, 359.
37. Bartram, M. E.; Koel, B. E. *Surf. Sci.* **1989**, *213*, 137.

38. Franken, P. E. C.; Ponec, V. *Surf. Sci.* **1975**, *53*, 341.
39. Solomun, T.; Christmann, K.; Baumgärtel, H. *J. Phys. Chem.* **1989**, *93*, 7199.
40. Solomun, T.; Baumgärtel, H.; Christmann, K. *J. Phys. Chem.* **1991**, *95*, 10041.

ACKNOWLEDGMENT

I acknowledge all people who have enriched my life.

GENERAL INTRODUCTION. ADSORPTION OF SMALL MOLECULES ON GOLD

Explanation of Dissertation Format

This dissertation contains results of research I have conducted in two different areas: 1) organometallic synthesis and reactivity 2) organometallic surface chemistry. In the synthesis and reactivity studies, sulfur coordination of thiophene and benzo[b]thiophene to the metal center in organometallic rhenium complexes is examined. In the surface chemistry studies, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is used to analyze the adsorption of several isocyanides on the surface of gold powder. The results are compared and contrasted to known organometallic chemistry.

This dissertation contains a general introduction and three papers. The general introduction is a literature review of the adsorption of small molecules on gold, and does not consider most electrochemical and interfacial studies using gold as a substrate. The following three papers contain the results of my research as it was or will be submitted for journal publication. Literature citations, tables, and figures pertain only to the papers in which they are included. Following the third paper is a general summary and the additional references cited in the general introduction.

GENERAL INTRODUCTION. ADSORPTION OF SMALL MOLECULES ON GOLD

Explanation of Dissertation Format

This dissertation contains results of research I have conducted in two different areas: 1) organometallic synthesis and reactivity 2) organometallic surface chemistry. In the synthesis and reactivity studies, sulfur coordination of thiophene and benzo[b]thiophene to the metal center in organometallic rhenium complexes is examined. In the surface chemistry studies, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is used to analyze the adsorption of several isocyanides on the surface of gold powder. The results are compared and contrasted to known organometallic chemistry.

This dissertation contains a general introduction and three papers. The general introduction is a literature review of the adsorption of small molecules on gold, and does not consider most electrochemical and interfacial studies using gold as a substrate. The following three papers contain the results of my research as it was or will be submitted for journal publication. Literature citations, tables, and figures pertain only to the papers in which they are included. Following the third paper is a general summary and the additional references cited in the general introduction.

END

**DATE
FILMED**

11/22/93